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FOREWORD

The role of the National Bureau of Standards (NBS) in the Interagency Energy/Environment R&D program, coordinated by the Office of Research and Development, U. S. Environmental Protection Agency, is to provide those services necessary to assure data quality in measurements being made by a wide variety of Federal, state, local, and private industry participants in the entire program. The work at NBS is under the direction of the Office of Environmental Measurements and is conducted in the Center for Analytical Chemistry and the Center for Radiation Research. NBS activities are in the Characterization, Measurement, and Monitoring Program category and address data quality assurance needs in the areas of air and water measurement methods, standards, and instrumentation. NBS outputs in support of this program consist of the development and description of new or improved methods of measurement, studies of the feasibility of production of Standard Reference Materials for the calibration of both field and laboratory instruments, and the development of data on the physical and chemical properties of materials of environmental importance in energy production. This report is one of a series issued every six months by NBS to provide information to the interagency Energy/Environment community on the status of methods, standards and data projects at NBS. Detailed project information is also provided in the Interagency Energy/Environment Research and Development Series.

C. C. Gravatt
Chief, Office of Environmental Measurements
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INTRODUCTION AND SUMMARY

This report describes work performed by the National Bureau of Standards (NBS) during the period, July 1978 to January 1979, under the Interagency Agreement (EPA/IAG-D8-E684) between the U. S. Environmental Protection Agency and NBS. This agreement covers the development of standards, methods, data, and instrumentation for the measurement of pollutants associated with energy production and use. The categories for this reporting period are represented by seven subagreement areas and are reported as follows:

80 BCKa - Energy Related Pollutant Measurement and Instrumentation Development

Under the task Energy-Related Water Pollutant Analysis Instrumentation work done with the cerium oxidative detection system for detection of phenols in the effluent of a liquid chromatograph was found to have a detection limit in the order of 10 ng phenol.

A new type of probe was also constructed for LC-MS interface, and use of iso-octane solvent was found to provide better results.

Studies done in the area of particulate analysis using secondary ion mass spectra from organic layers was applied to metallic particles.

In the laser-enhanced ionization (LEI) area, work focused primarily on improved refinements in the detection limit table, completion of a workable theoretical model to explain and predict experimental sensitivities and initial real sample measurements. LEI has been demonstrated for 18 elements in water at the sub-ppm level.

A project has been initiated this period on the development of Specific Immunoassays for Dinitrophenols in Water. DNA-conjugated proteins were produced to be used in the assay of purchased antisera. All antisera were assayed for specificity and titre by double gas diffusion and passive hemagglutination.

Under generation of Enhanced CARS Spectra of Organic Liquids in Capillary Waveguides, a new approach to analysis of organic compounds in liquid phase by Raman Spectroscopy has been developed. This technique can be adapted to a flow-through geometry coupled to HPLC, to improve the detection sensitivity of such systems.

80 BCLa - Energy Related Pollutants and Effects Monitoring and Associated Methods and Techniques Development

Under the task Development of SRMs for Stationary Sources Associated with Energy Production, results of analyses of two concentrations of NO_2 in air suggests a degree of stability suitable for a possible SRM. Under Development of SRMs for the Monitoring of Ambient Air Impacted by Emissions Resulting from Energy Production, study of feasibility of a low concentration sulfur dioxide-in-air compressed gas SRM has been completed. Due to instability of cylinders these gas mixtures would not serve as satisfactory SRMs, but possibly as secondary standards. Results obtained thus far show a slow decline in the concentration of nitric oxide, which would make mixtures in the concentration range of 1500 ppm unsuitable as SRMs. High concentrations of hydrocarbons were found in samples of carbon monoxide-in-air in cylinders lined with ceresin wax. The Computer-Operated Gas Analysis System (COGAS) has been modified and programmed to automatically analyze gas SRMs using gas chromatographic and other discontinuous analyzers. This system is now being used routinely for certification of all gas SRMs.

Under Develop Methods for Dispersal of Particulates on Filter Media and Methods for Determining and Controlling the Composition and Morphology of such Dispersed Particulates, work was concentrated on focused ion-beam sputtering. The larger machine used produced films whose composition was closer to the bulk target composition for Ca, Zn, and Pb. Results thus far indicate that ion acceleration voltage and ion-beam current determine the rate at which the sputtered secondary atoms leave the surface of the target, with no significant change in the film composition. Also, the addition of oxygen to the sputtering atmosphere appears to increase the content of ZnO and PbO in the films and decrease the amount of trapped argon in the films.

In work with the Particle Doppler Shift Spectrometer, progress has been made in the optical configuration, chamber design and in the data collection method. Also, for the first time, experimental data reproducibility matches the calculated Mie Scattering Curve features over a broad range of sizes.

The Ion Chromatograph instrument is now fully operational and has been used to analyze diverse sample types. In addition to sulfate and nitrate on glass fiber filters, other sample types analyzed were lyophilized oyster tissue, mechanical packing products, penetrant inspection materials, and waste oil.

A multi-element radioanalytical procedure for the simultaneous determination of As, Cr, Se, Sb, Cd, and Cu was developed and applied to a new Fly Ash SRM (1633a) and a new Sub-bituminous coal SRM (1635).

Preliminary analysis of a proposed Oil Shale SRM has been done by INAA for elements having intermediate and long-lived neutron irradiation products. Concentrations of 30 elements can be determined by INAA.

80 BCLb - Energy Related Air Pollutant Analysis Instrumentation

Under the task Development of an Instrument to Measure Airborne Sulfate Particulate Matter, field calibration results were compared with laboratory calibration results. Laboratory results showed considerable scatter, as well as systematic dependence on both SO_2 and relative humidity. In comparison to field calibration, in cases where sample is humidified and where SO_2 is present, agreement with laboratory calibration was found to be good.

80 BCLc - Energy Related Pollutant and Effects Monitoring and Associated Methods and Techniques Development

Under the task Radiocarbon as an Environmental Tracer, the results of the feasibility of mini-low level counting (LLC) of radiocarbon to distinguish anthropogenic from natural pollutant sources using only mg sample sizes, have been published. Further extension of the capabilities of this technique in terms of sample size, throughput and quality control have been undertaken. Experiments to apply the LLC method to two specific environmental problems have been undertaken: (a) in Oregon, to resolve the contribution of field and slash burning, wood stoves, natural emissions, fossil fuel combustion etc., to the total particle load; and (b) in Washington, a study to relate to the organic fraction in marine sediments. Activities directed toward measurement accuracy and model validity also have taken place. These applications served to increase the discriminating power of the LLC method through addition of chemical and physical selectivity.

Also development of capabilities through the use of accelerator mass spectrometry, large low-background proportional counters, stable isotope analysis, and trace gas radiocarbon analyses were also under investigation.

80 BCMA - Energy Related Pollutants and Effects Monitoring and
Associated Methods and Techniques Development

Under Energy Related Water Pollutant Standard Reference Materials, material for the Estuarine Sediment SRM is being analyzed by neutron activation analysis. Certification of a larger trace element-in-water SRM is in progress.

A report, entitled "The Quantitative Removal of the Alkali and Alkaline Earth Elements from the Trace Transition Elements in Sea Water Using Chelating Resin, and its Application to Analytical Instrumental Techniques," has been completed.

In the Inductively Coupled Plasma (ICP) technique, an operational approach was chosen to examine the statistical behavior of all channel-to-channel ratios during a normal analysis time period. Results indicate that, with proper choice of an internal standard, variability of response can be improved by a factor of two, provided that the signal-to-background ratio for the analyte element is ten or greater.

The procurement process for the production of an aqueous PAH SRM is presently in progress.

A direct injector is being developed that places a liquid sample on the head of the capillary column, bypassing the normal heated injection port, without adversely affecting chromatographic resolution, and has been found to be solute boiling point independent.

Data on the work related to the phenols-in-water SRM have shown that concentrations of phenol, o-cresol, and p-cresol remained constant throughout a 27-month study while the concentrations of 2-naphthol and 2,4,6-trimethylphenol were found to decrease with

time. The most probable cause for such losses were attributed to adsorptive losses to the walls of the glass ampoules. Also, radiation sterilization was found not to be a practical means of quenching biological activity.

80 BCN - Radiological Pollutant Quality Assurance

This work includes the completion of the calibration of natural isotopic uranium and continuation of the measurement of the half-life of plutonium-241. Fly Ash from combustion of eastern United States Coal is being assayed for radium-226 and radium-228. Tests on the radioactivity in SRM 1633, Trace Elements in Coal Fly Ash, continue. Gamma ray measurements using Ge(Li) for the determination of radium-228 are in progress. Six test sources have been provided to QAB and one result reported to NBS.

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APPENDIX-a-ENERGY RELATED POLLUTANT MEASUREMENT AND INSTRUMENTATION DEVELOPMENT

1. Energy-Related Water Pollutant Analyses Instrumentation

1.1 Development of Marker Compounds

Activity in this project must await development of the master analytical method by EPA/ERL/Athens.

1.2 Application of Selective Detectors to Liquid Chromatography

The cerium oxidative detection system is in principle a highly sensitive and fairly selective means for the detection of phenols in the effluent of a liquid chromatograph. Katz and Pitt (Anal. Lett., 5, 177 (1972)) first developed the "cerate oxidative monitor" for the detection of organic acids and other oxidizable components in body fluids. The column effluent is mixed with cerium(IV) reagent solution — cerium(IV) sulfate and sulfuric acid — by means of a magnetic mixer before entering the reaction section, which consists of coiled Teflon tubing (with an internal volume of 4 mL) immersed in boiling water. At a flow rate of 20 mL/min employed for the anion-exchange separation of aromatic acids, the residence time in the reaction section is about 12 minutes. A fluorometer monitors the fluorescence emission of the cerium(III) produced in the reaction.

Belkoff and Larose (J. Chromatogr., 99, 731 (1974)) employed a similar cerium fluorescence detector for the reversed-phase HPLC analysis of phenols in water. These workers used a peristaltic proportioning pump to add the reagents to the column effluent in order to reduce peak broadening in the HPLC separation. Using this system, concentrations of about 10 ppb of phenol could be detected, but the response generally decreased as substitution on the phenolic ring increased.

This detection system offers sensitivity because cerium III fluoresces strongly at 363 nm and selectivity (in addition to the chromatographic selectivity afforded by the column) because only oxidizable species are detected and reaction conditions can be optimized for a given class of compounds by controlling variables such as reaction time and temperature, and the nature and concentration of redox reagents.

The data given in Table 1 shows that detection limits obtained using ultraviolet detectors were lower with the added advantage that the integrity of the separation need not be sacrificed since no reaction coil is necessary.

TABLE 1

Comparison of the Sensitivities Afforded by Cerium Oxidative and Ultraviolet Detection of Phenols in Liquid Chromatographic Effluents

	<u>Ng injected into analytical system</u>			
	<u>phenol</u>	<u>p-cresol</u>	<u>o-cresol</u>	<u>2-naphthol</u>
Filter photometer 254 nm	2.6	5.5	3.7	0.4
Spectrophotometer 254 nm	12	23	14	4
Spectrophotometer at optimum wavelength	3.1 (270 nm)	3.6 (275 nm)	3.3 (270 nm)	1.7 (275 nm)
Cerium oxidative monitor	10	13	17	19

In a previous report we have described the use of an electro-chemical detection system for HPLC detection of phenols. This system has superior sensitivity (detection limit less than 0.1 ng) when compared with the cerium oxidative monitor and UV detectors and offers selectivity at least comparable to that afforded by the cerium oxidative monitor.

Though simple in principle and potentially sensitive and selective, there are other factors that detract from the utility of this system:

a) Cerium IV is unstable when in contact with fresh glass or heat and is oxidized to the fluorescent cerium III which causes background fluorescence.

b) The relationship between concentration and response is not always linear, probably due to the uncontrolled production of fluorescent oxidation products that also contribute to the signal measured.

c) The volume between the exit of the chromatographic column and the detector must be sufficiently large to allow

reaction of the phenols with the Cerium(IV), a sulfate.

We used a 2 mL reaction coil. This caused chromatographic band broadening and hence severe losses in resolution.

Because of combinations of these three factors, we found that we could not detect less than 10 ng phenol.

Further experience with the LC-MS interface probe has shown that the permanently-constricted tube is too easily plugged with particles in the liquid flow. A new type of probe was constructed (figure 1) with a constriction consisting of a 0.075 mm tungsten wire passing through the probe tube. The new probe tube has an OD of 1.0 mm and an ID of 0.10 mm. The tungsten wire has a football-shaped ball of silver solder on the end about 0.5 mm long and 0.3 mm in diameter. By moving the tungsten wire, the seating of the ball in the orifice at the end of the probe can be varied and the flow rate can be varied from approximately 10 $\mu\text{L}/\text{min}$ to less than 1 $\mu\text{L}/\text{min}$. This provides a convenient adjustment of the flow rate and will stop the influx of air when the probe is not in use. In use, the flow rate is set so that the pressure above the turbomolecular ion source pump is about 1×10^{-4} Torr.

It was discovered that less volatile compounds were not carried into the hot source effectively by the n-pentane solvent. We attribute this to vaporization of the solvent before it reaches the constriction of the probe tip. The use of iso-octane as the solvent gave much better results.

A liquid chromatograph was set up and the effluent was fed to the heated wire interface. The sample contained 3-methylnaphthalene, phenanthrene, fluoranthene, chrysene, and benzo(a)pyrene. An aminosilane column with 5 percent methylene chloride in iso-octane as the mobile phase was used for the experiment. Good separation of these compounds was obtained, and the mass spectrometer detected the first three satisfactorily. Detection limit for phenanthrene was estimated to be less than 100 ng injected into the chromatograph. It is expected that this will improve markedly when the mass-spectrometric parameters are optimized. The probe has been further modified to surround it almost to the tip with a copper heat sink. Calculations show that the tip temperature should not exceed 50 $^{\circ}\text{C}$ with this heat sink. Parts are on order which will enable us to measure source temperatures, and the source has been modified to incorporate heaters which will make it possible to control the source temperature.

LC-MS INTERFACE

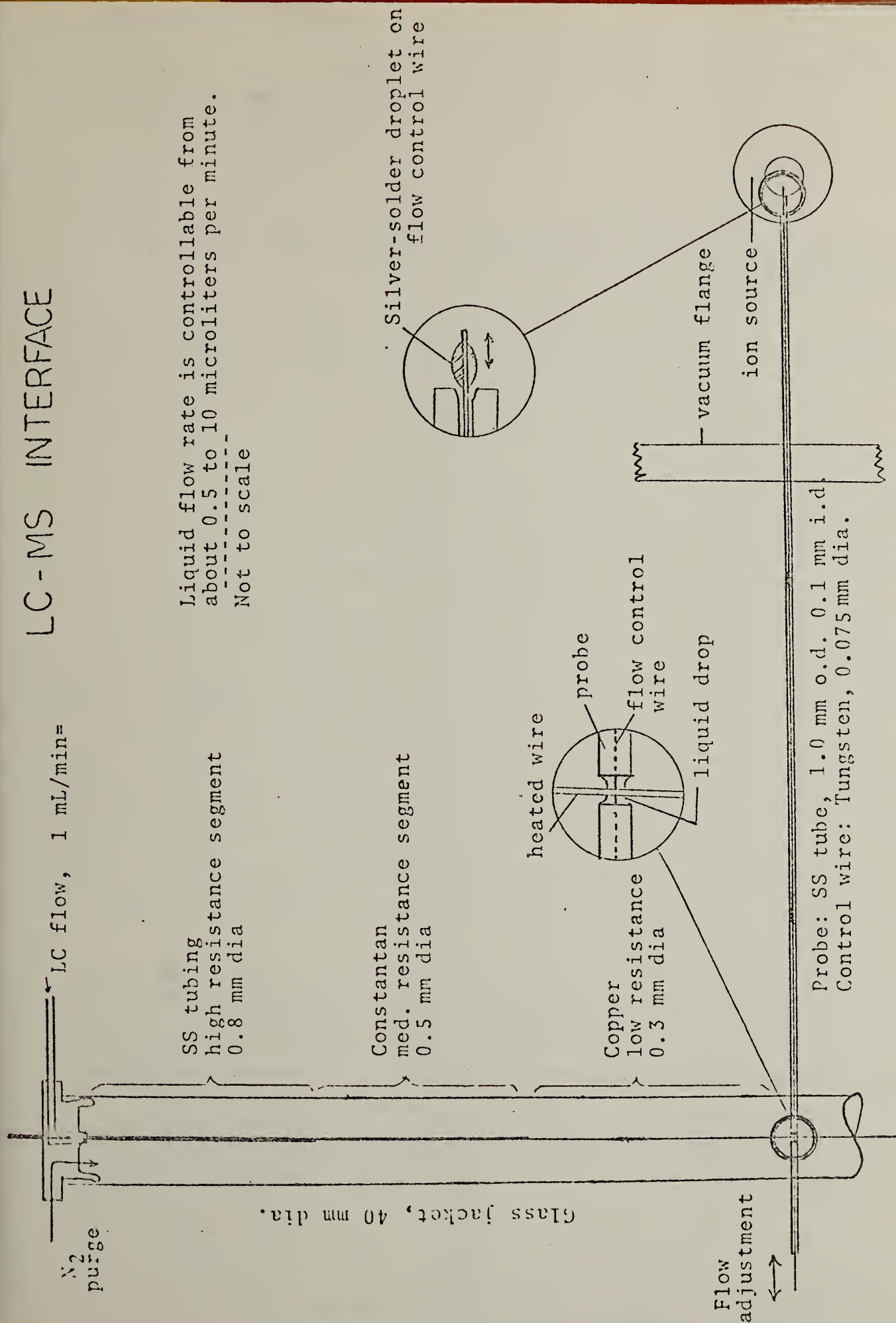


Figure 1. New type of LC-MS interface probe.

Consideration has been given to methods for a feedback control of the power input to the evaporator wire. This should make it possible to control the amount of evaporation on the wire so that 99 percent concentration can be obtained in spite of small input flow variations.

1.d Feasibility Study of Application of Particulate Analysis by Ion Microprobe

In the previous semi-annual report on the NBS/EPA Energy Environment Project (Sept. 1978) we reported preliminary results on the application of the ion microprobe (a focused beam form of secondary ion mass spectrometry) (SIMS) to the study of thin organic layers on substrates. Benninghoven and co-workers (University of Münster) had previously demonstrated that secondary ions corresponding to the parent organic compound as well as characteristic fragment ions could be successfully sputtered under ion bombardment conditions selected to minimize damage to a specimen: (a) inert gas primary ion such as Ar^+ ; (b) ion beam energy, typically 2 keV; and most important, (c) low primary ion beam current density, typically 10^{-9} A/cm^2 . These conditions are said to be "static SIMS" in which the specimen is unaltered by the measurement process. In order to obtain an adequate total signal with such a low current density, an area in the range $0.1\text{-}1 \text{ cm}^2$ must be bombarded. While Benninghoven's technique is satisfactory for the characterization of organic layers on a large substrate, or possibly on a large aggregate of particles, it is clearly not adequate for the characterization of organic layers on single particles.

In the previous report, we demonstrated the possibility of obtaining results similar to these reported by Benninghoven et al. under primary ion bombardment conditions which were more typical of the ion microprobe: (a) reactive gas primary ion, $^{16}\text{O}_2^+$; (b) high beam energy, 18.5 keV, and (c) primary ion current densities in the range 10^{-6} A/cm^2 . Parent compound and characteristic ion

fragments were detected from glycine on a nickel substrate and 5-fluorodopamine on a gold substrate.

These studies have been extended to the area of particulate analysis by measuring secondary ion mass spectra from organic layers applied to metallic particles (commercial purity nickel and silver) with a size range 20-60 μm diameter. The primary ion beam conditions employed were: (a) primary ion species, $^{16}\text{O}_2^+$; (b) beam energy, 9.50 keV (which corresponds to 4.25 keV monotomic oxygen bombardment); (c) current density, $2.8 \times 10^{-5} \text{ A/cm}^2$ (1 nA into a 60 x 60 μm square scan). Figure 2 shows a portion of the positive secondary ion mass spectrum obtained from atropine ($\text{C}_{17}\text{H}_{23}\text{NO}_3$) applied to a bulk nickel substrate. An ion signal was observed at 289 mass units which presumably corresponds to the parent ion. Most of the signals observed in the spectrum correspond to the substrate and its contaminants. Upon scanning the region from 90-120 mass units on a fresh area (offset portion), a large number of peaks corresponding to organic fragments are observed. This experiment points out the difficulty in obtaining useful spectra with a sequential spectral measurement. The destructive nature of SIMS leads to a destruction of the organic target. Figure 3 shows a limited mass scan in the range 90-120 mass units on a layer applied to a nickel particle. A pattern similar to that observed from the bulk target, Figure 2, is found. Peak-to-background ratios as high as 100:1 are observed for these ions in both the particle and in the bulk.

A similar experiment was conducted with 5-fluorodopamine applied to 20 μm diameter silver sphere. Spectra similar to the 5-fluorodopamine spectrum shown in the previous report (Figure 12) were obtained from the layer on the particle. The intensity of the parent ion at 171 mass units was found to be a strong function of the ion dose (bombardment time). Table 2 gives the intensity observed as a function of time on two replicate runs of 20 μm diameter particles.

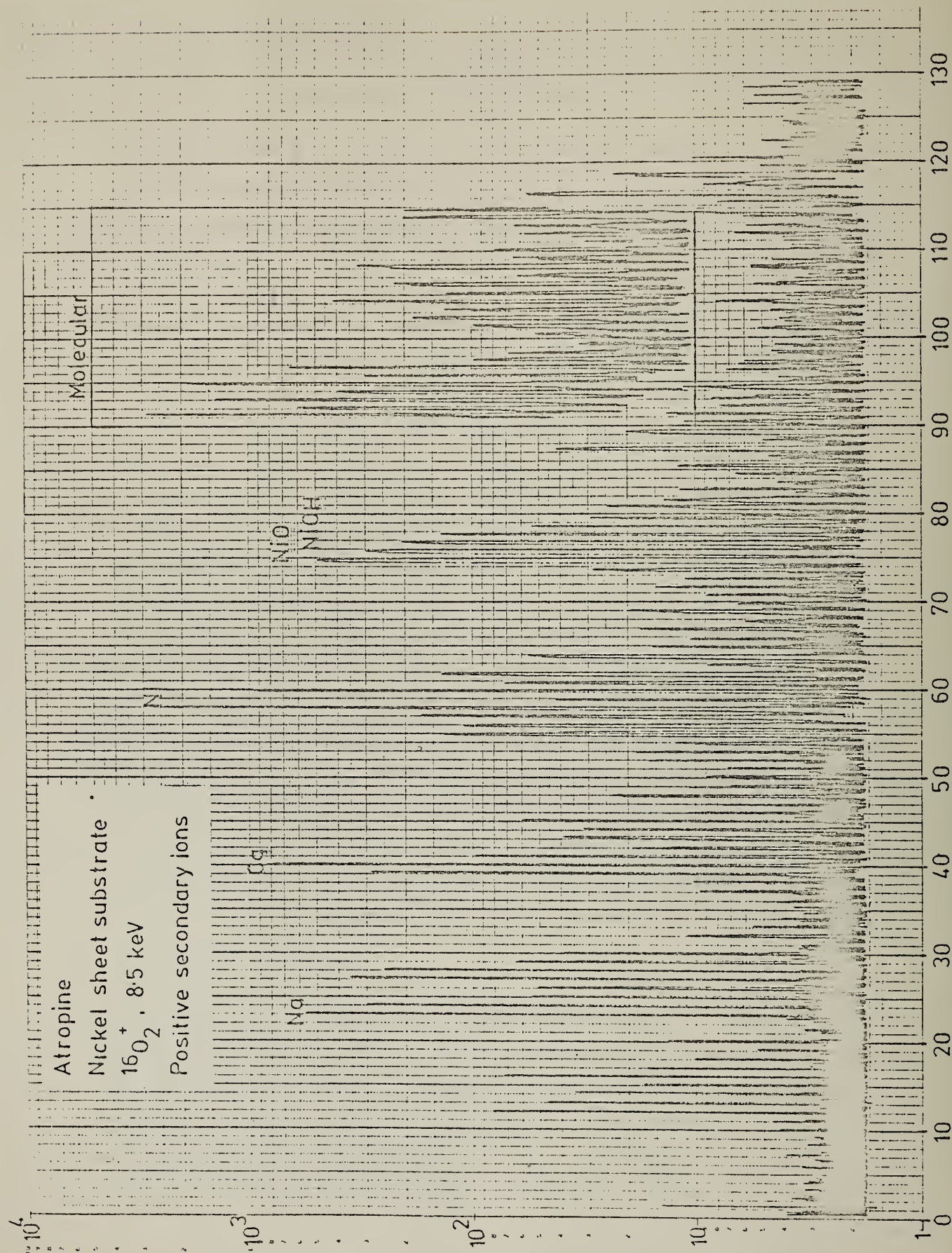


Figure 2. A portion of the positive secondary ion mass spectrum obtained from atropine applied to a bulk nickel substrate.

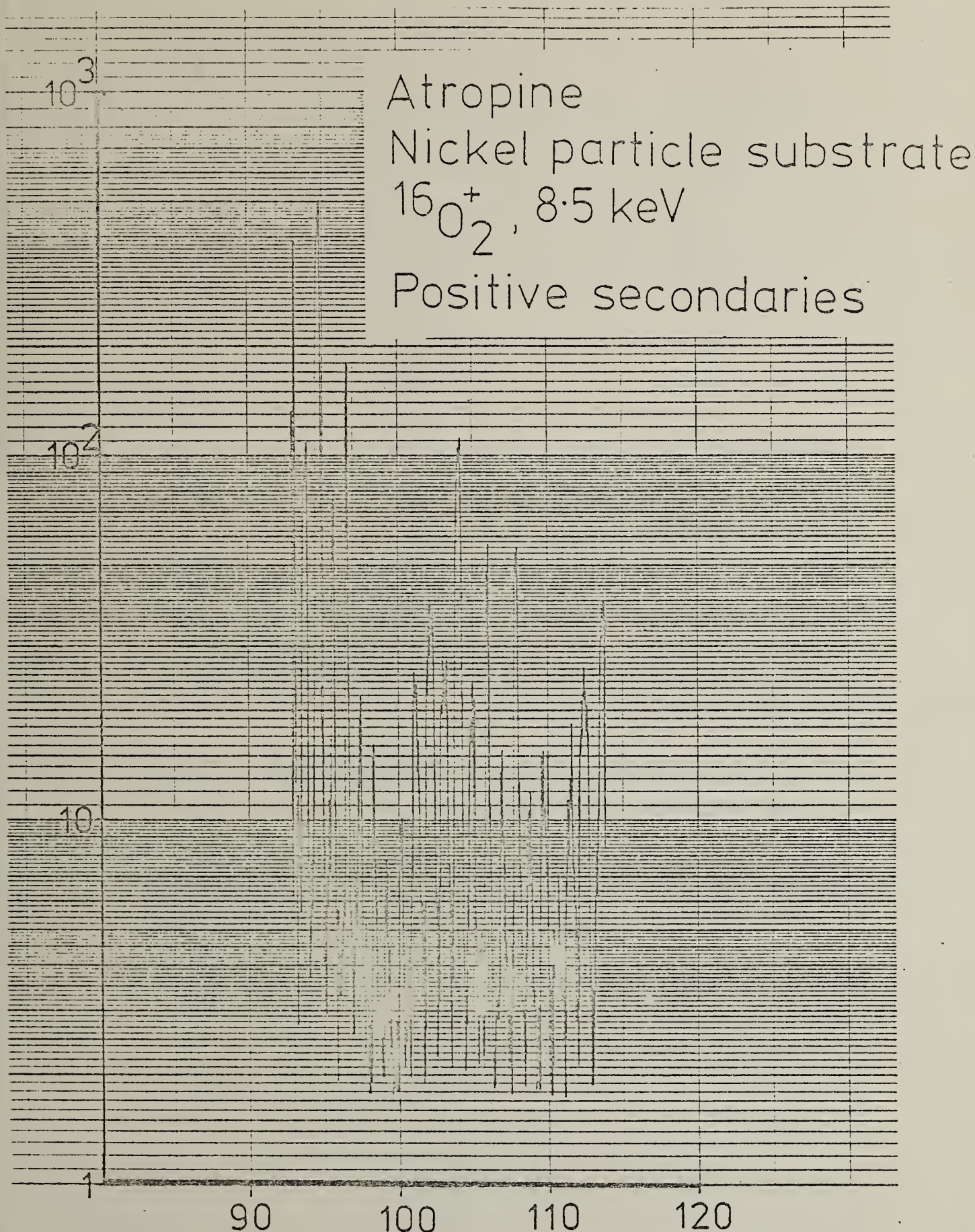


Figure 3. A limited mass scan in the range 90-120 mass units on a layer applied to a nickel particle.

TABLE 2

Intensity as a Function of Time on Two Replicate Runs of
20 μ m Diameter Particles

Time	Intensity at 171 mass units	
	sphere #1	sphere #2
2 seconds	1073	1052
4	246	495
6	179	351
8	135	253
10	106	151
12	127	128
14	104	103
16	86	98

This strong decrease in signal is due to (1) rapid sputtering of the organic layer and (2) beam damage of the organic compound.

Further experiments are being carried out to enlarge our experience with organic SIMS.

1.e Liquid Chromatography with Electrochemical Detection of Organometallic Compounds

A comprehensive report entitled, "Development of Methodology for the Measurement of Trace Organometal Species by Liquid Chromatography with Electrochemical Detection," has been completed and will be submitted to EPA for publication as an EPA Technical Report.

1.f Laser Enhanced Ionization

Introduction

Previous reports over the past three years have described the origination and early development of laser enhanced ionization for trace metal analysis in flames. The method uses a pulsed

or chopped tunable dye laser to selectively excite analyte atoms in the flame. A current passed through the flame via external electrodes and the burner head is seen to change in response to the laser excitation. The laser-induced current is separated from the dc background current by a simple RC network, amplified, and signal averaged following gated or synchronous detection. Sub-ng/mL detection limits and linear response over at least four orders of magnitude are currently obtained for over a dozen elements in water.

The second half of 1978 was devoted primarily to 1) continuing refinements in the detection limit table, 2) completion of a workable theoretical model to explain and predict experimental sensitivities, and 3) initial real sample measurements.

Limits of Detection

All of the limits of detection obtained to date are shown in Table 3, along with comparative limits by other flame techniques. Limits obtained during the period of this report (distinguished by footnote "c" in the table) are Ag, Ba, Bi, Ca, and Li.

As shown by footnote "d" in Table 3, twelve of the eighteen have equivalent or superior detection limits by LEI, in comparison to the best reported results by atomic absorption (AA), atomic emission (AE), atomic fluorescence (AF), or laser-excited AF. Of the thirteen elements with ionization potential (IP) ≤ 7.5 eV, only Ca, Cr, and K are better detected by another method. For these elements, much weaker transitions were used for the LEI measurement than for the other methods.

Of particular interest is the work done with lithium, detailed in Table 4. The 1 pg/mL (one part-per-trillion by weight) detection limit of Table 3 is the best yet measured for the method. The transition used was the traditional $2s\ ^2S-2p\ ^2P^\circ$ at 670.8 nm, as shown in Figure 4.

TABLE 5

Comparison of Detection Limits^a (ng/mL)
(46,85)

<u>Element</u>	<u>LEI</u>	<u>AA</u>	<u>AE</u>	<u>AF</u>	<u>Laser AF</u>
Ag (7.6) ^b	1 ^c	1	2	.1	4
^d Ba (5.2)	0.2 ^c	20	1	---	8
^d Bi (7.3)	2 ^c	50	20000	5	3
Ca (6.1)	0.1 ^c	1	.01	20	.08
Cr (6.8)	2	2	2	5	1
Cu (7.7)	100	1	0.1	0.5	1
^d Fe (7.9)	2	4	5	8	30
^d Ga (6.0)	0.07	50	10	10	0.9
^d In (5.8)	0.006 ^c	30	0.4	100	0.2
K (4.3)	1	3	.05	---	---
^d Li (5.4)	0.001 ^c	1	.02	---	0.5
^d Mg (7.6)	0.1	0.1	5	0.1	0.2
^d Mn (7.4)	0.3	0.8	1	1	0.4
^d Na (5.1)	0.05	0.8	0.1	---	0.1
Ni (7.6)	8	5	20	3	2
^d Pb (7.4)	0.6	10	100	10	15
^d Sn (7.3)	6	20	100	50	---
^d Tl (6.1)	0.09	20	20	8	4

^aLEI in C₂H₂/air flame; others in best flame available.

^bIonization potential in parentheses (eV).

^cNew LEI result (since last report).

^dLEI best method.

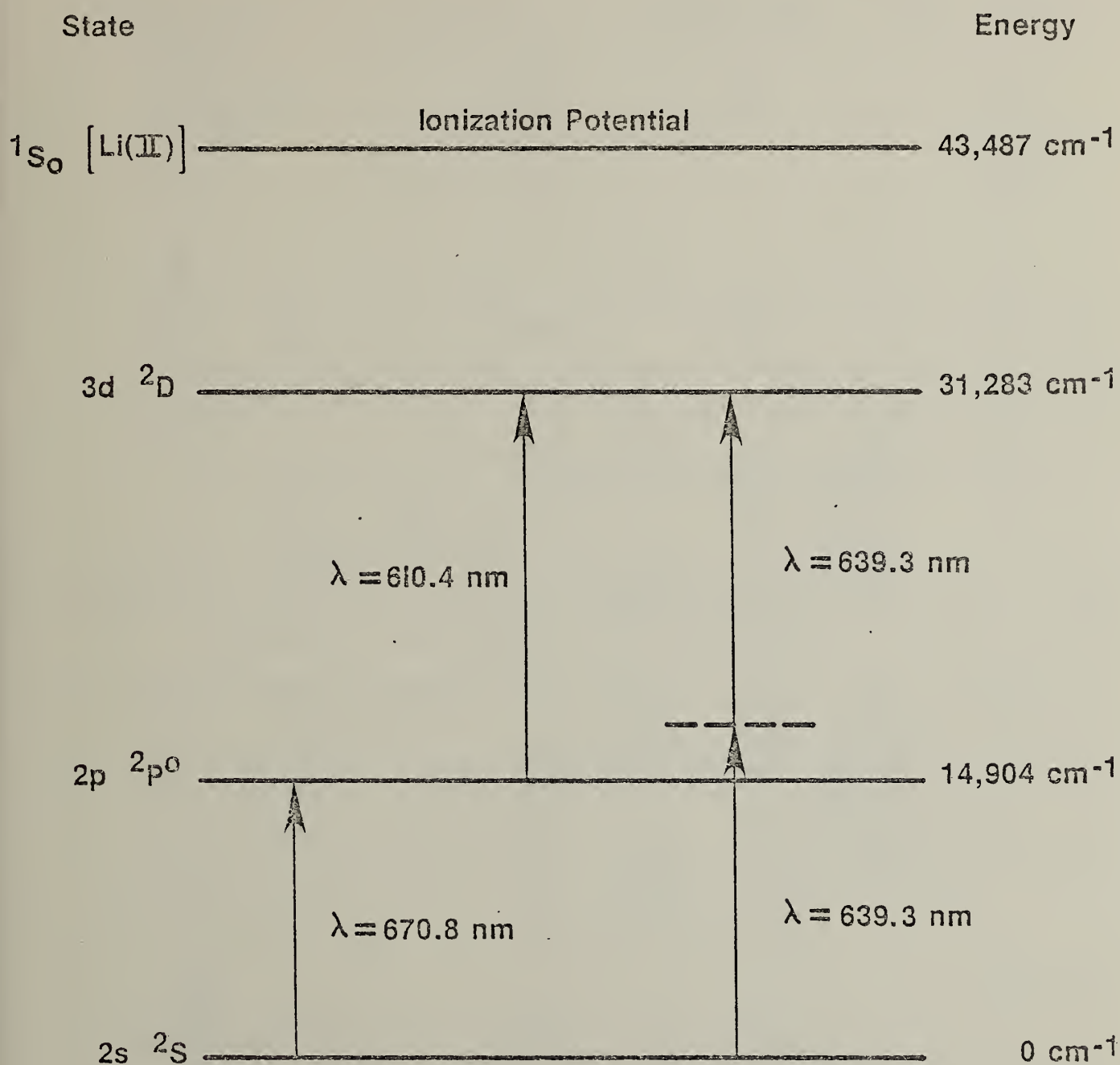


Figure 4. Partial energy level diagram of lithium.

TABLE 4

LEI Detection Limits for Three Transitions in Lithium

<u>Wavelength (nm)</u>	<u>No. Photons</u>	<u>Transition</u>	<u>LOD (ng/mL)</u>
670.8	1	$2s\ ^2S \rightarrow 2p\ ^2P^\circ$	0.001
610.4	1	$2p\ ^2P^\circ \rightarrow 3d\ ^2D$	0.012
639.3	2	$2s\ ^2S \rightarrow 3d\ ^2D$	0.4

A detection limit of 12 pg/mL for the excited $2p^2P^\circ \rightarrow 3d^2D$ transition at 610.4 nm illustrates the surprising sensitivity of the method for excited state transitions. The detection limit is only 12-fold worse than the ground state transition in spite of a Boltzmann population of $\sim 10^{-4}$ for the $2p^2P^\circ$ level. This effect is further discussed along with the mechanism studies below.

A final surprising result from lithium is the 0.4 ng/mL detection limit for the two photon $2s^2S \rightarrow 3d^2D$ transition using 639.3 nm light. Although of no practical value for Li detection, the result illustrates a method of extending laser enhanced ionization to elements of high ionization potential. Two UV photons — from a suitably high-powered frequency-doubled laser — could be used to excite energy levels up to ~ 10 eV above ground. The effective-single-photon wavelength of such transitions is in the vacuum UV, and cannot be reached directly with current laser technology.

Mechanism

The model for the production of LEI signal is based on the generalized energy level diagram of Figure 5. Levels 1, 2, and 3 represent the lower and upper levels of the optical transition, and the ion ground state, respectively. The E_i , n_i , and g_i are

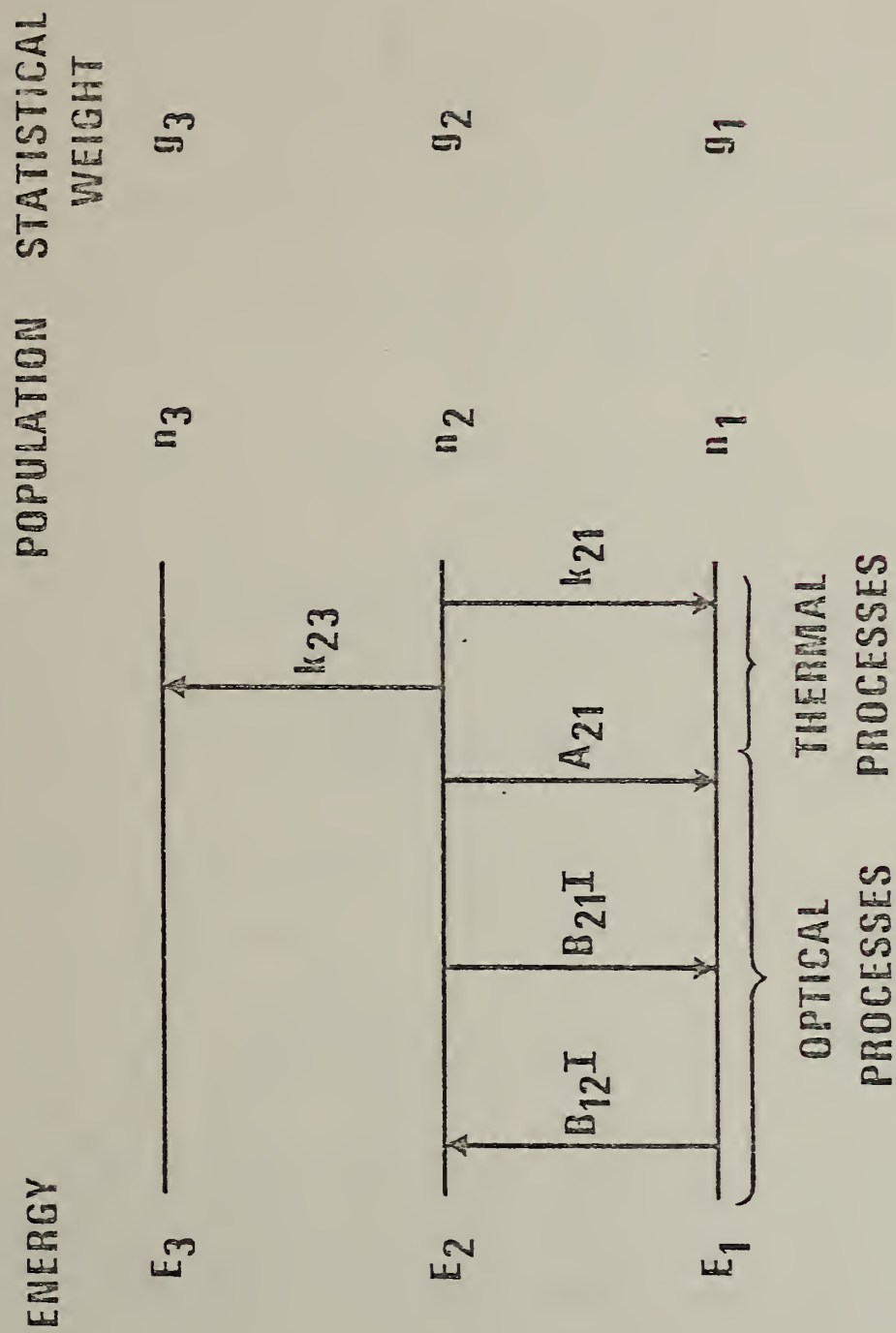


Figure 5. Generalized energy level diagram used to model LEL.

the corresponding energies, number densities, and statistical weights. (E_3 is thus the ionization potential, and n_3 the ion number density.) A_{21} , B_{12} , and B_{21} are the Einstein coefficients for spontaneous emission, absorption, and stimulated emission; I is the spectral irradiance of the laser; and k_{21} and k_{23} are collisional rate constants for quenching (de-excitation) and ionization from the excited state. Additional processes which occur are omitted as being of secondary importance.

The LEI signal current, S , is proportional to the rate of ionization from the excited state:

$$S \propto \frac{dn_3}{dt} = k_{23} n_2 \quad (1)$$

The excited state population, in turn, is a function of the laser intensity. In the absence of optical saturation,

$$n_2 \approx \frac{B_{12} I (N - n_3)}{A_{21} + k_{21}} \quad (2)$$

where $N \equiv n_1 + n_2 + n_3$ is the total analyte number density in the flame. Combining (2) and (1),

$$S \propto \frac{dn_3}{dt} = k_{23} \frac{B_{12} I (N - n_3)}{A_{21} + k_{21}} \quad (3)$$

If $n_3 \ll N$ for all time, that is, if the laser converts a trivial fraction of the analyte atoms to ions during the pulse, the peak signal current, S_m , can be seen from (3) to occur at the peak laser intensity, I_m , or

$$S_m \propto \frac{k_{23} B_{12} I_m}{A_{21} + k_{21}} N \quad (4)$$

which is linear in power, absorption coefficient, and ionization probability. A more general solution of (3), however, yields for the maximum current

$$S_m \propto N \left[\frac{k_{23} B_{12} I_m}{A_{21} + k_{21}} \right]^X \quad (5)$$

where $0 < X \leq 1$, and the less-than-linear response to power, absorption, and ionization probability results from "electrical saturation", i.e., the conversion of a significant fraction of the analyte to ions during the pulse.

The model of equation (5) was fitted to a data set of sensitivities (signal current per unit concentration) for 21 transitions in 14 elements. The fit yielded an exponent of $X = 0.63 \pm 0.05$ for equation (5), indicating that our flashlamp-pumped dye laser does indeed convert an appreciable fraction of the analyte to ions during the 1 μ s pulse. Figure 6 shows a plot of the experimental sensitivities versus the fitted sensitivities, with a spread of ≤ 1 order of magnitude for data over a range of > 4 orders of magnitude.

Application to Real Samples

The most severe problem encountered to date in the application of the method to real samples, has been the effect of high background ionization on the signal. When easily ionized elements are present in high concentration in the sample, they greatly increase the background ion/electron density in the flame. In such circumstances, the positive ion sheath, or space-charge, — which always exists near the cathode — is greatly enhanced, and the available electric field at the laser-excitation site is diminished.

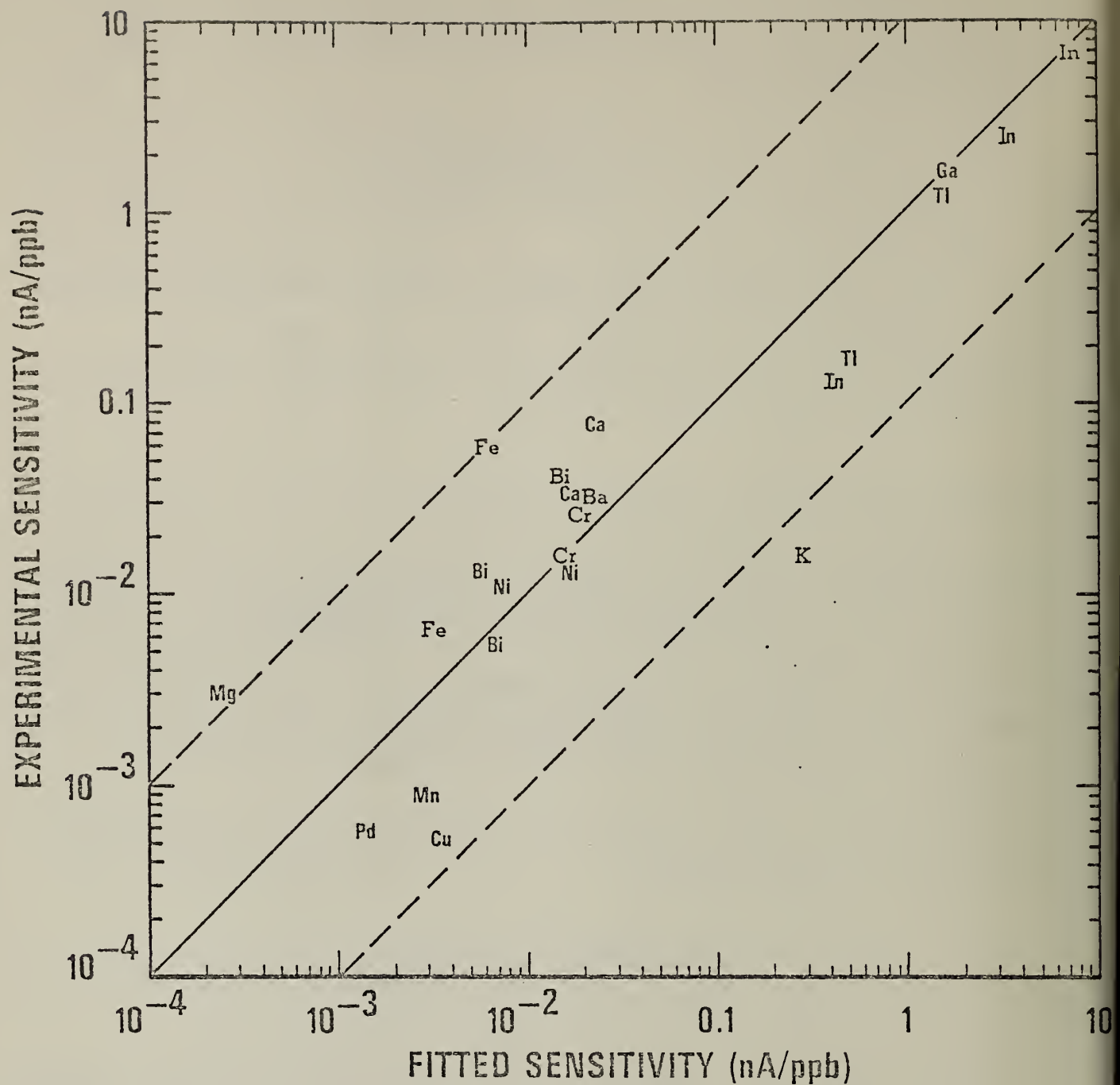


Figure 6. Comparison of experimental LEI sensitivities to the two-parameter theoretical fit value for twenty-one transitions in fourteen elements.

The extent of the problem when 1 mm diameter tungsten rods are used for the cathode is shown in figure 7, for a 100 ppb indium solution with increasing sodium matrix. During the present reporting period, an order of magnitude improvement was achieved — as shown in figure 8 — by the simple expedient of replacing the cathode rods with flat molybdenum plates. The positive ion sheath, and hence the matrix effect, is reduced by the inverse of the lightning rod principle — for a given applied potential, the field strength is less at a flat surface than at one of positive curvature.

The presence of easily ionized matrices is checked simply by comparing the background (dc) current with and without the sample being aspirated into the C_2H_2 /air flame. With the signal modified — but not eliminated — by easily ionized matrices, accuracy may be assured by using the method of standard additions. An alternative method, for small differences in background current, is to increase the fuel to the flame, thereby raising the background current to a point such that the change due to the sample is negligible. Then, the increased ion/electron density affects the sample and calibration standard measurements equally. Table 5 shows examples of three types of real sample measurement: 1) no matrix effect, neat calibration standards, 2) small matrix effect, fuel-rich flame used with neat standards, and 3) large matrix effect, standard additions used.

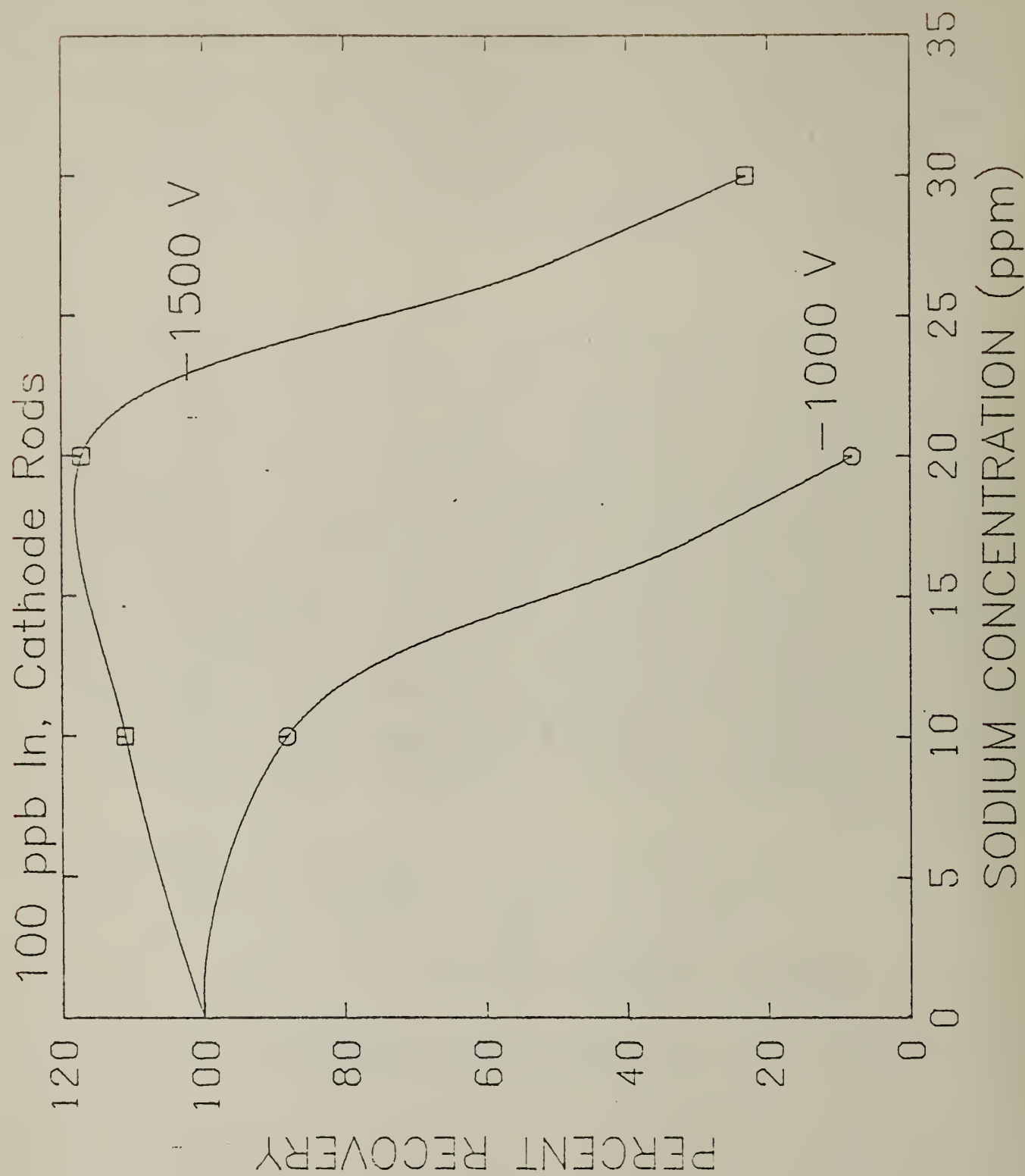


Figure 7. Percent recovery of 100 ppb indium LEL signal with increasing sodium matrix, using 1 mm diameter cathode rods.

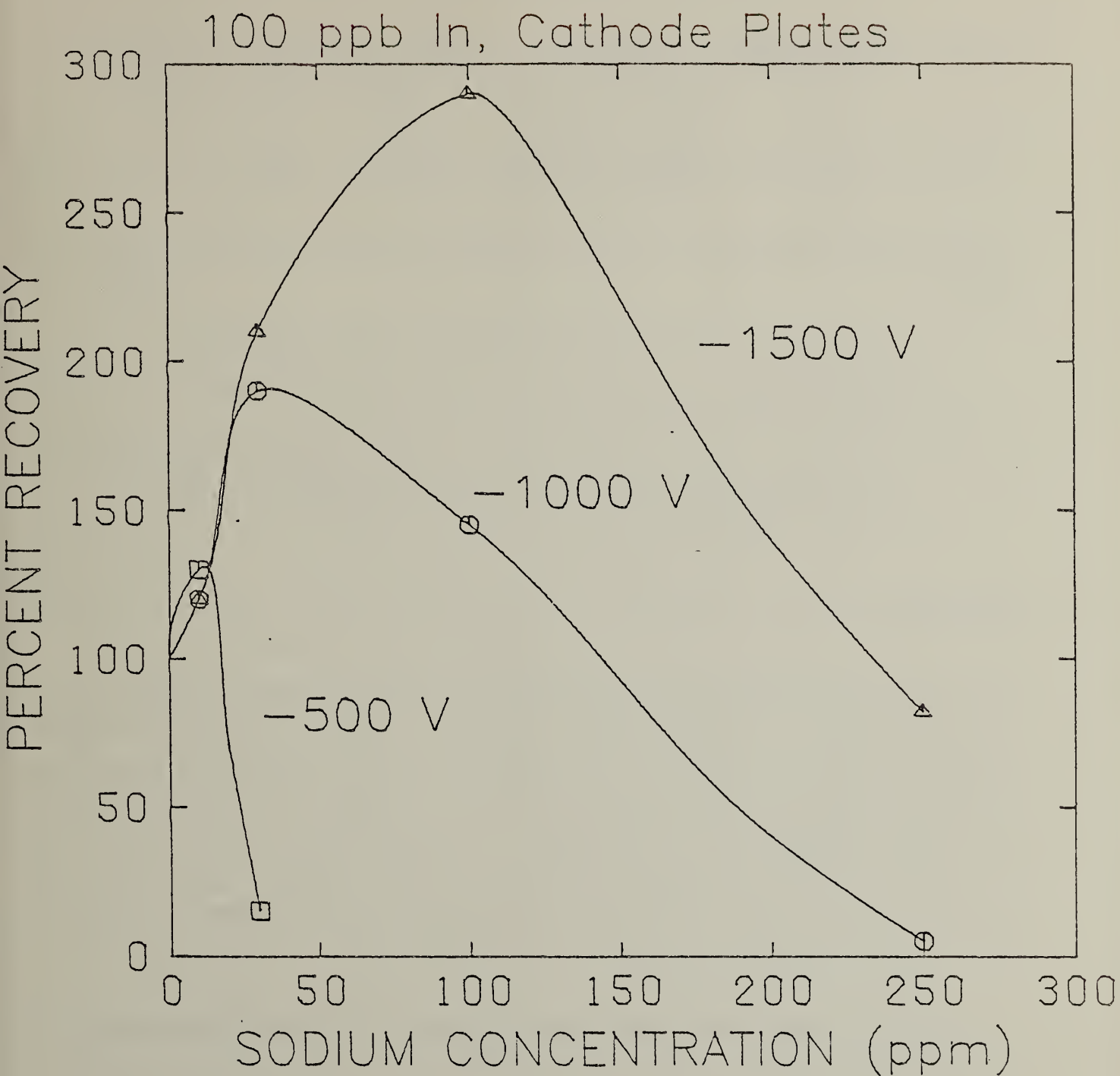


Figure 8. Percent recovery of 100 ppb indium LEI signal with increasing sodium matrix, using cathode plates.

TABLE 5

Representative Real Sample Measurements

<u>Element</u>	<u>Wavelength</u>	<u>Sample</u>	<u>LEI^a</u>	<u>Expected^a</u>	<u>Comments</u>
In	303.9	Ni-based Alloy	35	37	1
Mn	304.5	River Sediment	786	770	2
Mn	304.5	SRM 1261-Steel	6700	6600	3

^a
μg/g.

Comments:

1. No matrix effect; calibration via neat standard solutions.
2. High background current; calibration via standard additions.
3. Moderate background current; matrix effect compensated by using fuel-rich (high electron content) flame for both sample and neat standard solutions.

Conclusions

Laser enhanced ionization in flames has been demonstrated at sub-ppm levels for eighteen elements in water, with the best case extending to the part-per-trillion level. A model for the signal production mechanism has been shown to adequately describe observed sensitivities, and may be used to predict sensitivities for other elements and transitions. Matrix effects have been reduced an order of magnitude with a simple change in electrode shape, and five percent accuracy has been achieved with a small but representative selection of real samples.

Future directions will include 1) the extension to high ionization potential species with multiphoton or stepwise excitation, 2) further studies of optimum electrode structure for minimum matrix effect, 3) comparison of different laser systems, and 4) characterization of the electron/ion transport process.

1 Development of Measurement Methods for Non-Volatile Organic Pollutants in Water due to Energy Technologies

1.a Raman Microprobe Characterization of Trace Polynuclear Aromatic Hydrocarbons

No activity in this project during the present reporting period.

1.b Development of Specific Immunoassays for Dinitrophenols in Water

Because the sensitivity and selectivity of immunoassays for a variety of ligands offer many possibilities of separation and detection, we have started a project to develop assays for one of the priority pollutants, 2,4-dinitrophenol (DNP). Existing procedures evaluated at NBS have shown that gas chromatography and high performance liquid chromatography, while suited for analytical determinations of most of the toxic pollutants, are not as efficient in the separation and identification of the nitrophenols.

Immunoassays require highly specific antibodies produced in animals, usually rabbits or goats. Antibodies with specificity for small molecules such as DNP are made by chemically conjugating the DNP group to a specific protein and injecting the conjugate into the animal. Although commercially prepared antisera to DNP-proteins are available, we found that custom-prepared antisera were more economical and of higher quality.

We produced DNP-conjugated proteins to be used in the assay of purchased antisera, or to be injected as immunogens to produce specific antisera. Listed in Table 6 are the antigens produced.

TABLE 6

Dinitrophenylated Proteins Produced

<u>Protein</u>	<u>Conjugate</u>
Rabbit Albumin (RSA)	RSA-DNP ₆
	RSA-DNP ₁₁
	RSA-DNP ₁₆
	RSA-DNP ₁₈
	RSA-DNP ₂₅
Bovine Albumin (BSA)	BSA-DNP ₂₃
	BSA-DNP ₂₅
	BSA-DNP ₅₄
Bovine Gamma Globulin (BGG)	BGG-DNP ₆
Ovalbumin (OVA)	OVA-DNP ₂

Antisera with specificity for DNP were either purchased from stock or custom prepared for NBS. Two different conjugates were used as immunogens in the custom preparations. All antisera were then assayed for specificity and titre by two methods: double gas diffusion and passive hemagglutination. Results of these assays are listed in Table 7.

These data illustrate the wide variability in specificity and quality of the antisera. Choice of appropriate antisera for immunoassays depends on a combination of factors, with titre (reciprocal of greatest dilution factor giving positive response), or relative amount of specific antibody (IgG), being an important parameter for subsequent incorporation of the serum into a working assay.

TABLE 7

Specificity and Titre of Antiserum to
Dinitrophenylated Conjugates

<u>Source</u>	<u>Gel Diffusion</u>	<u>Passive Titre Hemagglutination</u>			
	vs 0.5 mg/mL BSA-DNP ₂₃	<u>UNCONJ</u>	<u>BSA</u>	<u>BSA-DNP₂₃</u>	<u>RSA-DNP₁₈</u>
<u>Commercial</u>					
Lab A - Rabbit	1:4	10	10	160	10
Lab A - Goat	0	40	40	160	80
Lab B - Rabbit	1:4	0	320	640	80
<u>Custom-Produced</u>					
3A-1	1:8	0	160	1280	80
3A-2	1:16	0	0	1280	20
3A-3	1:8(+)	10	40	640	80
3B-1	0	10	10	10	10
3B-2	0	10	10	10	10

The ultimate goal of detecting parts per million (ppm) or parts per billion (ppb) of DNP in water will have to be achieved with very specific antibody used in a competitive binding type of assay. Immunochemical tests performed with the crude antisera using free DNP as an inhibitor of gel diffusion or passive hemagglutination demonstrated the problem. Using gel diffusion, the minimum free DNP detectable was 1×10^{-2} mol/L or about 2,200 ppm. Passive hemagglutination was inhibited by 6.3×10^{-4} mol/L or about 140 ppm. Neither inhibition method was sensitive enough to be considered as a viable assay for free DNP in water.

Inhibition studies, however, were useful in directing the ultimate method of assay procedure. Binding characteristics of serum #3A2

were studied by inhibiting gel reactions with a variety of DNP-labeled compounds. Affinity for the DNP ligand is weak, while affinity for the homologous antigen (BSA-DNP₂₃) is strongest in the following series:

DNP<p-aminobenzyl-L-glutamate-DNP<glycylglycylglycine-DNP<lysine-DNP<BSA-DNP₂₃.

Development of a ligand binding assay using tritiated DNP (³H-DNP) was started. Whole antisera was used in the initial study as we developed optimum conditions for separation of the bound vs. free fractions of labeled ligand. Charcoal separation (0.1% Norit) was 96 percent effective in separating the free ligand from the bound. Similarly, a purchased commercial preparation was evaluated for separating the bound ligand on the IgG antibody from the free ligand in solution. Both methods showed some promise for separation but were not satisfactory for assay because the binding of the ligand to the specific antisera was not significantly different from binding to the normal control sera. This non-specificity may be due to the presence of many other proteins in the sera. We have now fractionated the sera to isolate the immunoglobulin, IgG. These fractions are being evaluated and will be bound to plastic tubes for use as solid-phase reagents. We have developed for this procedure protein detection methods suitable for detecting microgram quantities of IgG bound to tube surfaces.

Better sensitivity of a solid phase assay may depend on displacement of a different ligand than ³H-DNP. We are procuring a small amount of ¹⁴C-DNP-lysine to be used in the method.

Additional experiments are now being carried out to optimize the binding of IgG onto either polypropylene or polystyrene tubes. These will be followed by binding experiments with the labeled DNP compounds. We also anticipate measuring quenching of antibody fluorescence as it binds with the DNP hapten.

1.c LC-MS, Covered under section 80-BCK-a, 1.c.

1.d LC-EC, Covered under Section 80-BCK-a, 1.b.

1.e Ion-Probe, Covered under section 80-BCK-a, 1.d.

1.f Generation of Enhanced CARS Spectra of Organic Liquids in Capillary Waveguides

Recently we have developed a new approach to analysis of organic compounds in liquid phase by Raman Spectroscopy. Enhancements of up to a factor of 130 have been demonstrated in the Coherent Anti-Stokes Raman Spectroscopy (CARS) output from a sample in a liquid-filled dielectric waveguide compared to the signal obtained from the same material in a cuvette. The waveguide CARS experiments show this large enhancement in sample volumes of about 0.75 μL . Thus, the advantages of CARS, namely fluorescence rejection, low average power input, and spatial filtering can be maintained in the waveguide in very small volumes. This technique can be adapted to a flow through geometry to be coupled to HPLC, for example, to improve the detection sensitivity of such systems.

SO-BCL-a-ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND
ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

1 Development of SRMs for Stationary Sources Associated with
Energy Production

1.a NO₂ in Air Gas Blend SRMs

The results obtained on periodic analyses of two concentrations of nitrogen dioxide in air (reported in September 1978 semi-annual report) suggests a degree of stability which may be satisfactory in terms of an SRM. However, the small number of available samples makes it difficult to fully evaluate these mixtures over the desired concentration range of 250 to 2500 ppm. Consequently, a large number of cylinders at nominal concentrations of 250, 500, 1000, and 2500 ppm have been ordered. The mixtures at 250 and 2500 ppm should be received and a preliminary analysis completed by March 31, 1979. The 500 and 1000 ppm mixtures should be received and analyzed by June 30, 1979.

Subsequent analyses may be necessary to establish stability but the number of such subsequent analyses and the time period involved will depend to a great extent on the results of the preliminary analyses.

1.b SO₂ in N₂ SRMs

No work was done during the last six month period in this project. We must await funds for purchase of material.

1.c NO in N₂ SRMs

Work on this project will be completed in the next few months but is being funded by MVMA.

1.d O₂ in N₂ and CO₂ in N₂ SRMs

No work was done during the last six month period in this project. Material has been ordered (2 and 10 percent O₂ in N₂).

2 Development of SRMs for the Monitoring of Ambient Air Impacted by Emissions Resulting from Energy Production

2.a SO₂ in Air

The study of the feasibility of a low concentration sulfur dioxide in air compressed gas SRM has been completed. While it appears that some individual aluminum cylinders containing mixtures of sulfur dioxide in air at concentrations below one part per million (ppm) may have reasonable stability, similar cylinders in the same concentration range were found to be unstable. The instability appears to depend on the condition of the individual cylinder, and is of sufficient magnitude that such mixtures would be unsatisfactory as SRMs. However, the rate of loss of sulfur dioxide is such that cylinders containing mixtures of sulfur dioxide may serve as satisfactory laboratory standards, provided that the concentration is periodically determined on a relatively short time basis.

Another problem which was observed with these mixtures results from adsorption of small quantities of sulfur dioxide in the cylinder valves. The aluminum cylinders employed in this study were equipped with stainless steel valves. It was necessary to flow the mixture out of the valve at either a high flow rate or for a very long period of time in order to reach equilibrium. For example, a sample flowing at a rate of 1.3 L/min had not reached equilibrium after a period of 30 minutes. Conversely, a mixture in the same concentration range generated with a

permeation tube and flowing at 1.2 L/min reached equilibrium within 9 minutes. Flow through the valve at a rate of 2.3 L/min would require about 20 minutes to reach equilibrium.

It was possible to minimize all external factors in the slow equilibration process by proper choice of materials and by conditioning but it was not possible to eliminate the influence of the cylinder valve.

Thus, it appears unlikely that gas mixtures of this sort would serve as satisfactory SRMs. However, with proper selection and monitoring of individual cylinders, and with an awareness of the critical nature of the flow through the valve it is possible to use them as secondary standards.

NO₂ in Air

There have been no further developments in the gas industry that would offer any hope for preparing concentrations of nitrogen dioxide in air at concentrations below the 1 ppm level that would be satisfactory as SRMs.

NO in N₂

Further measurements of the four mixtures previously analyzed confirm the anomalies reported earlier. It appears from the results obtained thus far, that there is an initial slow decline in the concentration of nitric oxide. As the pressure within the cylinder decreases, nitric oxide previously adsorbed on the walls is desorbed and a slight rise in concentration occurs. This effect will be confirmed by further analyses during which all four samples will be bled to approximately atmospheric pressure. If the effect is real it will mean that mixtures in this concentration range would not be suitable as SRMs.

2.b CO in Air

Further examination of samples of carbon monoxide in air in cylinders lined with ceresin wax has revealed the presence of hydrocarbons at concentrations higher than expected. Previous batches of carbon monoxide in nitrogen contained in wax lined cylinders did not contain detectable quantities of hydrocarbons. Substitution of aluminum cylinders for the wax-lined steel cylinders appear to have resolved this problem. Analysis of 26 samples of 10 ppm carbon monoxide in air, prepared as a single lot, indicates complete homogeneity within the limits of precision of the method of analysis ($\pm 0.12\%$ relative). This is rather good evidence of the essential stability of the mixture in aluminum cylinders.

2.c Automation of Gas Analysis

The Computer Operated Gas Analysis System (COGAS) has been modified and programmed to analyze gas SRMs using gas chromatographic and other discontinuous analyzers. The system works as well for discontinuous analyzers as it does for continuous analyzers, such as non-dispersive infrared instruments. It is now used routinely for certification of all gas SRMs, with the exception of permeation tubes and high concentration sulfur dioxide in nitrogen standards.

Work is in progress to expand COGAS from a twenty to a fifty cylinder capability. In addition, work is in progress, within a different program, to construct a system to automate the calibration of permeation tubes utilizing similar hardware and programming as was developed for COGAS.

3 Develop Methods for Dispersal of Particulates on Filter Media and Methods for Determining and Controlling the Composition and Morphology of Such Dispersed Particulates

3.a NBS-SRM 1648 Urban Particulate Matter

SRM 1648 has been certified (see Appendix I).

3.b Synthetic Ground Glasses Deposited on Filters

There has been no activity in this project during the past six-month period.

3.c Thin Glass Films Produced by Focused-Ion Beam Sputtering

In the previous report covering the period from January 1 to July 1978 we described our work in the following areas: (1) Deposition of NBS-SRM 1648 particulate matter, (2) Grinding of synthetic glasses prior to deposition on filters, and (3) thin films of glasses prepared by the focused ion-beam sputtering technique. From July 1978 to December 30, 1978 our work was directed totally to the preparation and characterization of glass films prepared by sputtering and the results of this work are described in this report.

The 17.8 cm glass target used in these sputtering experiments was fabricated and ground to a thickness of 2 mm at NBS. The elemental composition of the target was the same as used in previous work described in the report of July 1977 and consisted of 36.0% SiO_2 , 18.0% CaO , 20% ZnO , and 26% PbO . A series of experiments was performed in which the major instrumental parameters, such as ion-acceleration voltage and ion-beam current, were systematically varied to determine their effect on the elemental composition of the glass films. Table 8 is a summary

TABLE 8

Summary of Instrumental Conditions Employed (Large Machine)^a

Date	Set No.	No. in Set	Time hrs.	Filament	Plasma Generator	Ar mm Hg	O ₂ mm Hg	Ion-Accl. Voltage	Neut.	Ion-Current	Ion Focus
5/4/78	1	3	4.2	16-24.5/5.5	60/2.6	7x10 ⁻⁸	1x10 ⁻⁸	700-800	46/2.6	45 mA	90/40
5/5/78	2	7	4.4	16-24.5/5.5	60/2.6	7x10 ⁻⁸	1x10 ⁻⁸	700-800	46/2.6	45 mA	90/40
5/5/78	3	6	4.3	16-24.5/5.5	60/2.6	7x10 ⁻⁸	1.1x10 ⁻⁸	700-800	46/2.6	45 mA	90/40
6/19/78	4	5	2.5	16-24.5/5.5	60/2.6	7x10 ⁻⁸	1x10 ⁻⁸	1,000	46/2.6	85 mA	90/40
6/26/78	5	5	3	24.5/5.5	60/2.6	7x10 ⁻⁸	1x10 ⁻⁸	1000-1500	46/2.6	119 mA	90/40
6/29/78	6	5	3	16/5.2	90/.78	7x10 ⁻⁸	1x10 ⁻⁸	1,500	46/2.6	70 mA	150/10

^aLarge machine used is instrument B in 1978.

of the instrumental conditions employed. Table 9 is the results of the analysis of the glass films measured by x-ray fluorescence spectrometry. Some commercial thin films containing single elements were used as standards, including previously measured thin sputtered films (e.g. F-20, F-23). It should also be noted that in the present instrument employed, a 12% oxygen, 88% argon atmosphere was maintained for sputtering the target, prior to deposition on the substrates for at least two hours. For purposes of comparison the results of previous work described in the July 1977 report (i.e., instrument A) are tabulated along with the results of this work (i.e., instrument B).

Comparison of the results in Table 10 indicate that the larger instrument (B) used in 1978 produced films whose composition was closer to the bulk target composition for Ca, Zn, and Pb. The value for silicon is about the same for either instrument. It is interesting to note that although preferential sputtering for the light elements Si and Ca and a decrease for Zn and Pb still exists, the absolute value of the relative difference of all elements from the bulk composition is approximately the same. From Table 9 it appears that varying the sputtering parameters (voltage and ion-current) does not affect the film composition appreciably. The best agreement was obtained in sets 2 and 3 which were done in the same day under identical conditions. Set 5 showed the largest deviation for Pb and was prepared under the highest ion-beam current obtainable. Even under these extreme conditions the Pb composition of set 5 was only 10-15% less than the average value of the other sets.

These findings are important in that the ion acceleration voltage and ion-beam current principally determine the rate at which the sputtered secondary atoms leave the surface of the target with no significant change in the film composition.

TABLE 9

Composition of Glass Films Determined by
X-ray Fluorescence Spectrometry

Set No.		<u>% SiO₂</u>	<u>% CaO</u>	<u>% ZnO</u>	<u>% PbO</u>
1	AV.	48.7	21.4	14.5	21.2
	S _x ^a	3.0	1.2	0.5	0.7
2	AV.	46.6	22.4	14.9	20.8
	S _x	1.0	0.5	0.3	0.5
3	AV.	46.4	21.7	14.7	20.3
	S _x	1.1	0.4	0.3	0.4
4	AV.	43.5	22.4	14.2	18.4
	S _x	0.9	0.5	0.3	0.3
5	AV.	45.6	23.8	13.3	16.7
	S _x	0.2	0.1	0.1	0.1
6	AV.	47.5	25.4	15.4	19.5
	S _x	0.6	0.3	0.2	0.2
Overall Average		46.4	22.9	14.5	19.5
	S _{AV} ^b	0.7	0.6	0.3	0.7
Bulk Comp.		36.0	18.0	20.0	26.0

^aS_x is one standard deviation of the average value of each set.

^bS_{AV} is one standard deviation of the overall average of all the sets.

TABLE 10

Comparison of the Average Composition of Sputtered
Films Using Two Different Instruments A and B

<u>Instrument</u>	<u>% SiO₂</u>	<u>% CaO</u>	<u>% ZnO</u>	<u>% PbO</u>
A, 1977				
AV.	43.7	32.0	7.8	8.8
B, 1978				
AV.	46.4	22.9	14.5	19.5
Bulk Comp.	36.0	18.0	20.0	26.0
% Rel. Δ, ^a A	+21	+78	-61	-66
% Rel. Δ, ^a B	+29	+27	-28	-25

^aPercent relative difference between the film and bulk composition,
i.e., $\frac{\text{Film-Bulk}}{\text{Bulk}} \times 100$.

Although there still exists an appreciable difference between the target and the film composition, this is not considered important as long as the film composition obtained from any particular target is constant and reproducible. The results obtained thus far indicate that this is indeed the case. The addition of oxygen in the sputtering atmosphere appears to increase the content of ZnO and PbO in the films, and also greatly decreases the amount of trapped argon in the films. Additional experiments are now in progress in which the amount of oxygen in the sputtering atmosphere is being varied to quantify its effect on the film composition.

Future Work

Further work is planned in 1979 to fabricate additional glass targets of different elemental composition of interest to EPA and to prepare thin films from these. Of great interest to us is the fabrication of a target containing sulfur as sulfate in a borate matrix. The results of this work will be reported in the next semi-annual report.

4 Particulate Physical and Chemical Characterization

4.a.b.c Particle Doppler Shift Spectrometer (PDSS)

Progress has been made in the optical configuration, the chamber design, and the data collection method. Calibration of a commercial optical particle counter was performed. Also, for the first time, experimental data reproducibly matches the calculated Mie scattering curve features over a broad range of sizes. These Mie features are reflected in relatively large differences in the intensity of light scattered as a function of particle diameter. This match of Mie features serves as an internal standard to better than 0.2 μm accuracy for homogeneous, spherical aerosol particles of four to twenty μm diameter.

Before reviewing these advances, some comment on items in the January 1978 and September 1978 Semi-annual Reports is in order. First, methylene blue was found to be unsatisfactory for solid size standard particles. The imaginary part of the index of refraction was so large as to obliterate the Mie features. Second, a vacuum system was implemented on the PDSS, and the predicted increase in particle velocity was observed for 2 μm diameter latex spheres. We have not yet pursued this further because of difficulties in introducing the aerosol sample into the vacuum, and because of a lack of Mie features for smaller particles. Third, computer matching Mie features to experimental data by searching the index of refraction and density space has turned out not to be practical. Index or density, but not both, can be determined by matching the Mie features. We have found it better to start with a substance of known index and density, determined from the bulk material.

The new PDSS optical configuration increases the size resolution and data rate by collecting light from a larger scattering volume

and from a more narrowly defined scattering angle. A viewing microscope is included to give a visual check of the scattering volume.

The new chambers are designed to suppress convection and wall interference effects as were present in previous chambers. The new design also includes a Brewster window and a sample collection surface (bottom window) that can be changed during a run.

An entirely new data collection scheme is being developed. The spectrum analyzer collects the summation of many spectra in the usual way for the Mie feature calibration. Simultaneously, the computer accumulates the peaks (particles) by size, from each spectrum, in real time. In this fashion, the size distribution can be measured directly in terms of equivalent aerodynamic diameter regardless of the shape of the aerosol particles. For the case of homogeneous spheres made from well characterized material, the equivalent aerodynamic diameter can then be related to the optical diameter using the Mie feature calibration.

The match of Mie features mentioned above has been obtained with a spray of pure di-octyl phthalate (DOP) from an atomizer. This match is being used as a standard for investigation of DOP aerosol generated by the following generators for which slight mismatches are observed: the vibrating orifice generator, the atomizer at higher flow rates, and aerosol spray cans. These mismatches may be due to various effects which we can detect because of the sensitivity of the Mie feature calibration technique.

Before the above match was obtained, a comparison of a commercial optical particle counter with the PDSS was performed at very low particle concentration. The twelve particle sizes used generated by the vibration orifice generator, were between four and eight μm diameter. Results of this work are to be published.

4.d.e Development of Air Supported Plasmas

No activity in this project during the last six months.

5 Particulates on Glass Fiber Filters

5.a.i. Ion-Chromatography

A recent acquisition to the Inorganic Analytical Research Division of the Center for Analytical Chemistry at NBS is the Ion-Chromatograph (Dionex Corp., Sunnyvale, CA). Acquired in January 1978 and put into operation in March, the instrument is now fully operational and has already been used to analyze several diverse types of samples, ranging from oysters to air filters.

The Ion-Chromatograph is a new tool for trace analysis in analytical chemistry that is based on the ion-exchange chromatographic separation of ionic species, followed by conductimetric detections. The high background conductance associated with the eluent is made negligible through use of a suppressor resin column. The method is ideally suited for inorganic anions, but is also applicable to low molecular weight organic acids, as well as some cations and cationic species. Ion-chromatography has already shown great promise toward the solution of complex trace analysis problems, in particular, the speciation and quantitation of species existing in, or are conducive to conversion to, anionic forms. The potential of ion-chromatography to determine several species simultaneously is especially attractive to the field of microanalysis. A typical analysis of a suitably prepared sample containing fluoride, acetate, chloride, nitrite, phosphate, bromide, nitrate, sulfite, and sulfate, takes about 25 minutes (Fig. 9). The minimum detection limit for these common anions under standard conditions is about 0.5 ppm, with a precision of 1 to 3 percent. The minimum detection limit can

ION - CHROMATOGRAPHY STANDARD

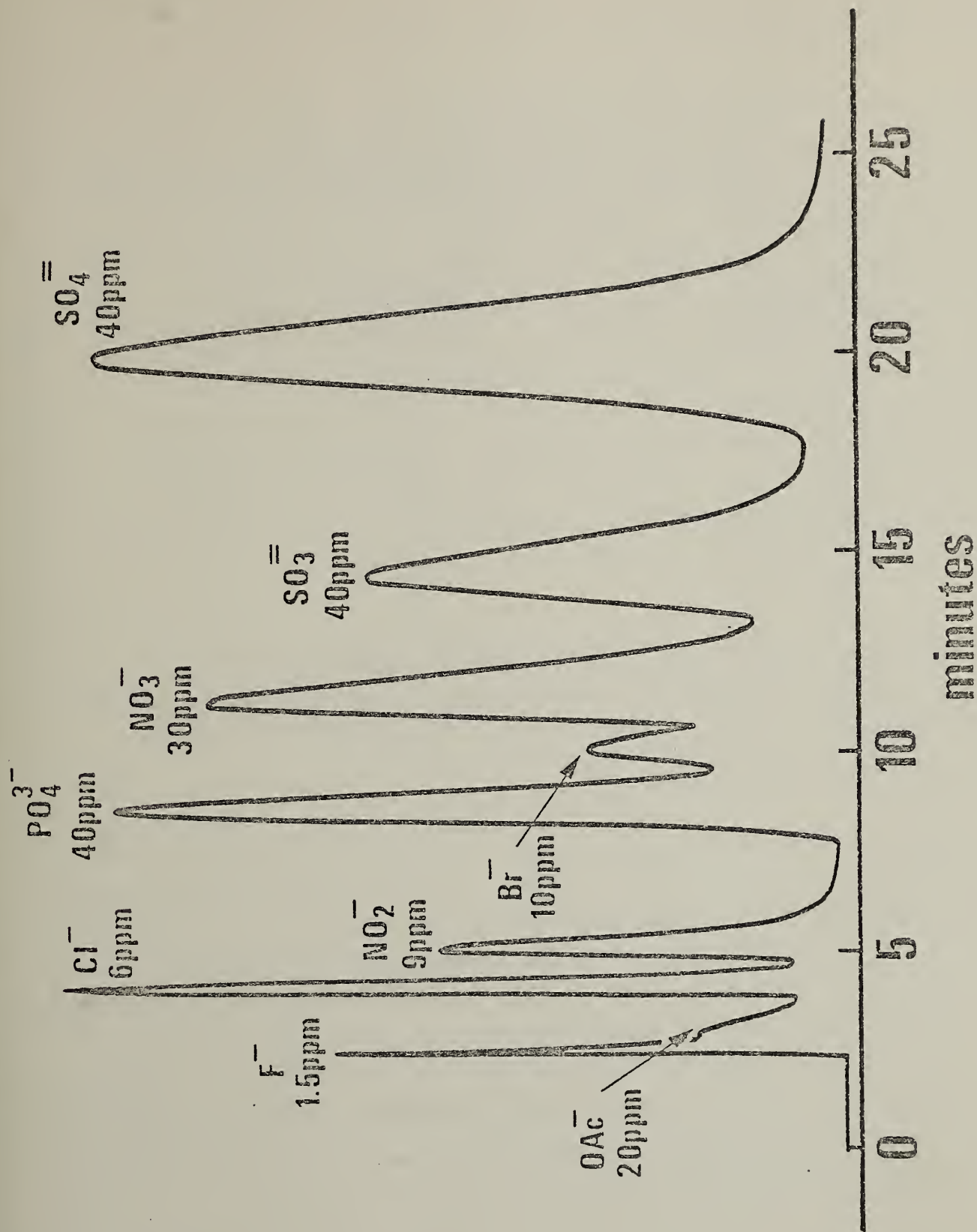


Figure 9. Typical analysis of a suitably prepared sample containing fluoride, acetate, chloride, nitrite, phosphate, bromide, nitrate, sulfate, and sulfite.

be extended 10 to 100-fold through use of larger sample loops or concentrator columns. Current research indicates that, under different chromatographic conditions, iodide can also be determined with a minimum detection limit of about 0.2 ppm.

Since ion-chromatography is a chromatographic (separation) technique, speciation (e.g. sulfide/sulfite/sulfate; nitrite/nitrate) is possible, and is primarily dependent on the method of sample preparation. Aqueous samples, such as rain water, fresh water, and sea water, may be analyzed with little or no sample manipulation; solids must be solubilized, generally by standard microchemical techniques (dissolution, sonification, extraction, fusion, digestion, or combustion). Such manipulations may, of course, alter the rate of these species in the original sample. Much research is being concentrated in this laboratory in optimizing sample preparation methods and chromatographic parameters for simultaneous multi-component analyses in real samples.

The types of samples analyzed to date in this laboratory by ion-chromatography include lyophilized oyster tissue, mechanical packing products, glass fiber filters, penetrant inspection materials, and waste oil.

The scope of the oyster project was to detect and quantitate as many anionic species as possible in lyophilized oyster tissue. It was intended to look at both the anions soluble in water, and the anions resulting from a suitable combustion technique. For the solubles, six peaks were detected, and identified by reference to a standard solution. Quantitation was possible only to a very approximate level for the soluble anions (Table 11) (Figure 10). Very good quantitative information on chloride and sulfur was obtained after combustion of the oyster tissue in a Schöniger oxygen flask (Table 12) (Fig. 11).

TABLE 11

Solubles in Oysters

Peak Identification and Approximate Quantitation

<u>Peak</u>	<u>Probable Species</u>	<u>Approximate Concentration</u>
a	F^{-}	<0.02%
b	Cl^{-}	1.1%
c	PO_4^{3-}	0.7%
d	Br^{-}	<0.09%
e	NO_3^{-}	<0.13%
f	$SO_4^{=}$	0.19%

SOLUBLES IN OYSTER

E3//30%//Log//650//0.5

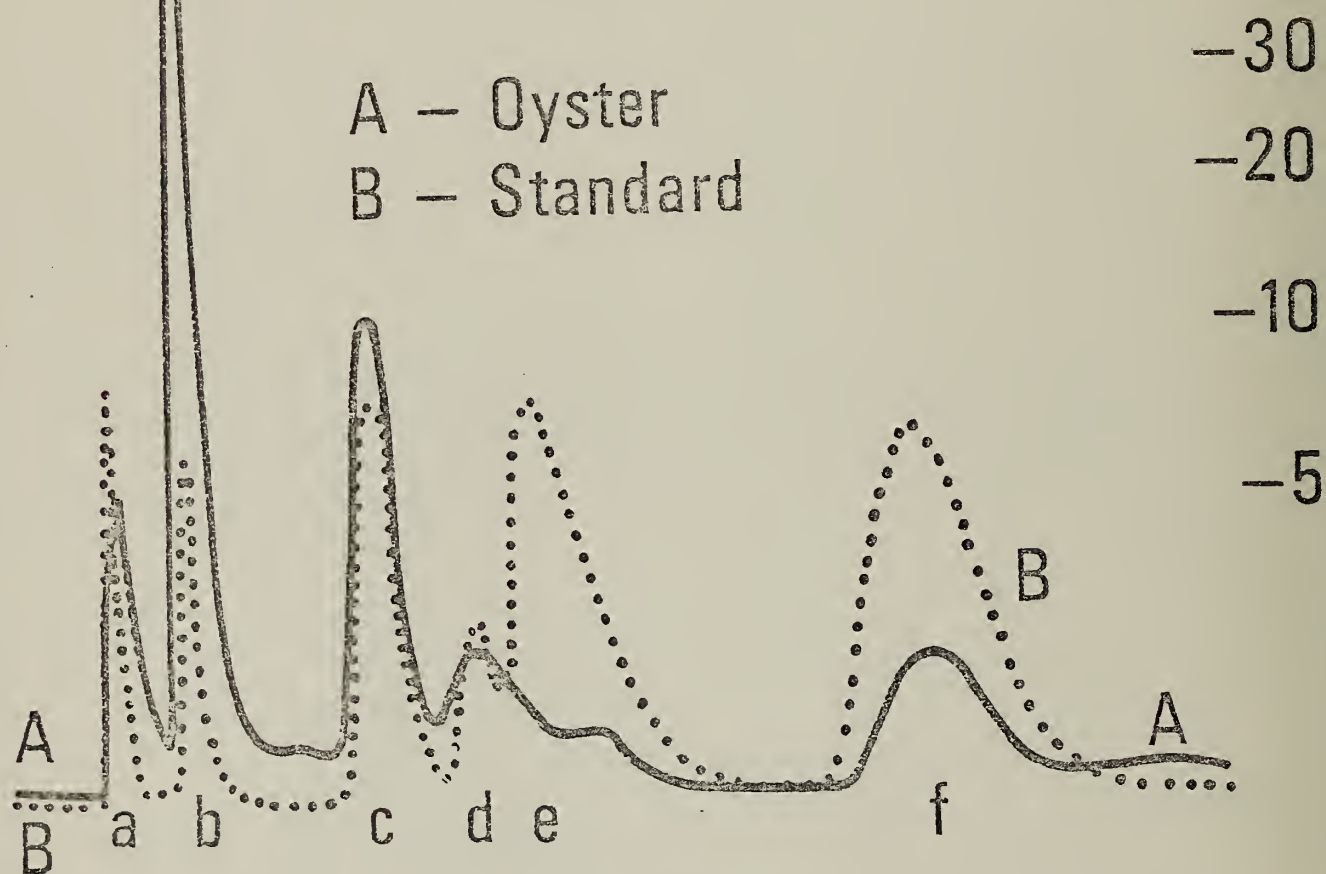


Figure 10. Solubles in oysters.

TABLE 12

Chloride and Sulfur (as Sulfate) Concentrations in
Oyster SRM as Determined by Ion-Chromatography
After Schöniger Flask Combustion

<u>Sample Wt.</u>	<u>Scrubber Soln. Wt.</u>	<u>Chloride</u>	<u>Sulfate</u>
11.59 mg	20.10 g	1.034%	2.201%
24.36	20.07	1.032	2.259
19.80	20.00	1.057	2.244
12.05	19.99	1.010	2.253
18.32	19.99	1.037	2.258
17.33	20.20	1.051	2.278
26.67	19.99	1.038	---
20.11	20.02	<u>1.013</u>	<u>2.300</u>
		Mean 1.034%	2.256%
		Std.Dev. 0.016	0.031
		Rel.Std.Dev. 1.6 %	1.4 %

OYSTER

17.33 mg combusted in Schöniger flask
Scrubber solution 20.20g H₂O

Conditions:

for Sulfate E3//25//10//650//0.5

for Chloride E3//10//30//650//0.5

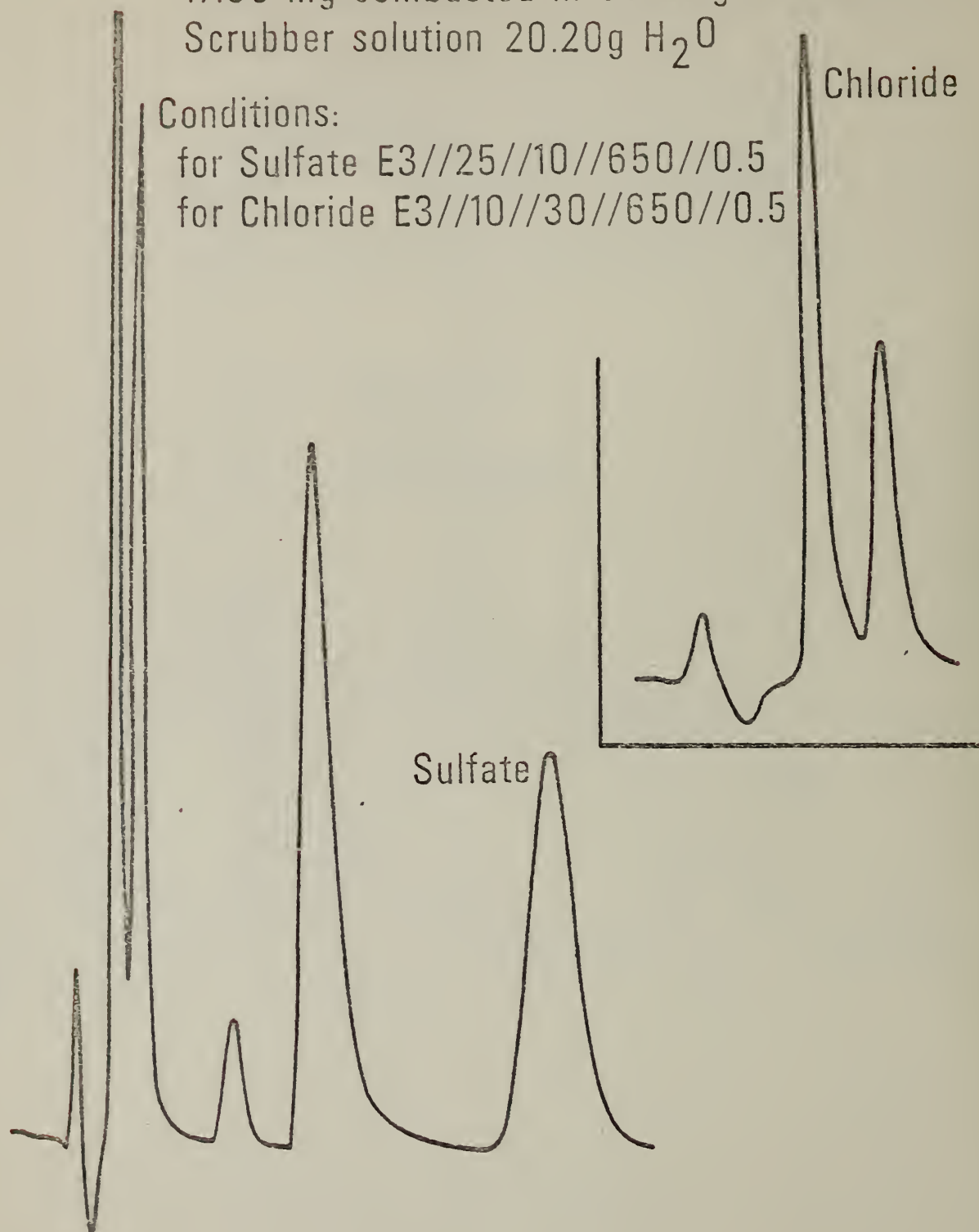


Figure 11. Chloride and sulfur concentrations in oyster SRM as determined by ion chromatography after Schöniger flask combustion.

Leachable chlorides have been determined in mechanical packings (Teflon asbestos or graphite-asbestos composites) at the 10-100 ppm level. Nitrate and sulfate on glass fiber filters were determined for use as standards in air-particulate analysis (Table 13). Penetrant inspection materials used to detect faults in steel welds were analyzed for fluoride and chloride in conjunction with an ASTM round-robin. These materials were combusted in a Parr oxygen bomb prior to analysis. The level of chloride in fourteen different samples ranged from 3 to 1800 ppm, and fluoride from 0.5 to 200 ppm. Waste oil has also been analyzed by ion-chromatography for chloride and bromide after digestion by the sodium alcoholate method.

These five types of analyses briefly illustrate the types of samples amenable to analysis by ion-chromatography. Obviously, ion-chromatography has tremendous potential in the determination of heretofore uncertified species in the NBS environment and energy related Standard Reference Materials presently available (such as coal and bovine liver); as well as in new materials (such as the air-particulate filter strips). It is anticipated that the potential of the ion chromatograph will be fully exploited in trace analysis application to such areas of activity at NBS.

TABLE 13

Summary Analysis of Filter Strips for Nitrate and Sulfate
by Ion-Chromatography

<u>Series</u>	Nitrate		Sulfate	
	Mean	(S.D.)(R.S.D.)	Mean	(S.D.)(R.S.D.)
II-BL	1.5 μ g	(1.0)	2.3 μ g	(1.5)
II-A	100.3 μ g	(2.6)(2.6%)	502.6 μ g	(8.9)(1.8%)
II-B	1002 μ g	(16)(1.6%)	2002 μ g	(29)(1.5%)
II-C	2513 μ g	(43)(1.7%)	6939 μ g	(109)(1.6%)

5.a.ii Lead, Sulfate, and Nitrate on Filter Media

This SRM consists of 416 mm x 203 mm strips cut from glass fiber filters. These filters are of the type commonly used with high volume samplers for the measurement of atmospheric particulates. Solutions containing known amounts of potassium sulfate, potassium nitrate, and lead nitrate were prepared gravimetrically and aliquots of 25 μ L were pipeted onto the filter strips. Four aliquots were transferred to each filter in all cases except sample I-C which required five aliquots. The pipets were calibrated by weighing similar aliquots transferred into weighing bottles.

The filters were prepared in a clean room and allowed to air-dry before packaging in glassine envelopes. The filters were prepared in groups of 100 and the proper number of aliquots were dispensed into weighing bottles at the beginning and end of each loading sequence, to monitor the performance of the pipet.

The values calculated from the composition of the solutions and the quantities delivered by the pipets are in agreement with the analytical values. The nominal values are shown in the attached table 14. Six hundred filters at each level were prepared.

Work on Pb on GFF has started and is being steered toward development of an SRM.

Work on sulfate and nitrate also being steered toward development of SRMs.

TABLE 14

Nominal Values of SO_4 , NO_3 , and Pb on Filters

- - - - - ug/filter - - - - -			
<u>Filter Group</u>	<u>Sulfate</u>	<u>Nitrate</u>	<u>Lead</u>
Blank	0	0	--
I-A	500	100	--
I-B	2000	1000	--
I-C	7000	2500	--
Blank	--	--	0
II-A	--	--	100
II-B	--	--	300
II-C	--	--	1500

6 Urban Air Particulate Washington D. C. Sample

Work begun under this task to be reported on in next semi-annual report.

7 Develop SRMs for Coal Conversion Processes and Materials Balance Determinations

A multi-element radioanalytical procedure for the simultaneous determination of As, Cr, Se, Sb, Cd, and Cu was developed and applied to two NBS environmental standards, a new Fly Ash SRM (1633a) and a new Sub-bituminous Coal SRM (1635). An inorganic ion exchanger coupled to a solvent extraction system was used for the selective separation of these elements from neutron-activated matrices. The results are shown in Tables 15 and 16.

During dissolution of the Fly Ash SRM, large losses of chromium were observed. These losses were mainly due to the large amounts of HF needed for complete dissolution of the highly silaceous matrix and the fact that chromyl fluoride is extremely volatile.

Because of the losses of chromium, instrumental neutron activation analysis was used to analyze chromium in the Fly Ash.

TABLE 15

NBS SRM Sub-bituminous Coal (1635)

<u>Element</u>	<u>Certified Values^a</u>	<u>This Work^a</u>
As	0.42 ± 0.15	0.44 ± 0.05
Sb	(0.14)	0.12 ± 0.01
Se	0.9 ± 0.3	0.82 ± 0.04
Cr	2.5 ± 0.3	2.48 ± 0.08
Cd	0.03 ± 0.01	0.029 ± 0.003
Cu	3.6 ± 0.3	3.56 ± 0.18

TABLE 16

NBS SRM Fly Ash (1633a)

<u>Element</u>	<u>This Work^a</u>
As ^b	146 ± 6
As	152 ± 8
Sb	6.07 ± .61
Se	11 ± 1
Cr ^b	200 ± 7
Cd	1.06 ± .16
Cu	121 ± 6

^aUnits in ug/g.

^bDetermined by Instrumental Neutron Activation Analysis.

A preliminary analysis of the proposed Oil Shale SRM has been done by instrumental neutron activation analysis (INAA) for elements having intermediate and long-lived neutron irradiation products. The observed elemental concentrations are listed in Table 17, along with the estimated uncertainties obtainable by INAA. The concentrations of approximately thirty elements can be determined by INAA. In general, the concentrations of trace elements in the Oil Shale is very similar to those in SRM 1632a (Coal).

Arrangements are being made to have some of the Oil Shale sterilized. This sterilized material will be compared to some unsterilized Oil Shale to determine if there are any changes in the elemental concentrations of volatile elements. Some of the sterilized and unsterilized material will be given to the Organic Analytical Research Division to look for differences in the concentrations of organic compounds.

TABLE 17

Approximate Elemental Concentrations in Shale Oil
as Determined by INAA

	<u>μg/g</u>	<u>Estimated Uncertainty (%)</u>
Na	1.6 ^a	<5
K	1.0 ^a	<5
Rb	63	<5
Cs	3.4	<5
Ba	540	5-10
Sc	4.6	<5
Cr	32	<5
Fe	1.8 ^a	<5
Co	9.0	<5
As	64	<5
Se	3.5	5-10
Sb	2.8	5-10
La	20	<5
Ce	34	<5
Sm	2.5	<5
Eu	0.52	<5
Yb	0.85	<5
Lu	0.18	<5
Hf	1.5	5-10
Ta	0.30	10-15
Th	4.7	<5

^aValue is given as percent, all other values are in μg/g.

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 1648

Urban Particulate Matter

This Standard Reference Material is intended for use in the calibration of methods used in the chemical analysis of atmospheric particulate matter and materials with similar matrices. The material is atmospheric particulate matter collected in an urban location.

The certified values are based on measurements of 6 to 30 samples by each of the analytical techniques indicated. The estimated uncertainties include those due to sample variation, possible methodology differences, and errors of measurement (see Preparation and Analysis). The certified values are based on a sample size of at least 100 mg of the dried material. The material should be dried at 105 °C for 8 hours before use.

Element	$\mu\text{g/g}$	Element	Weight %
Arsenic ^c	115 \pm 10	Iron ^{a b c}	3.91 \pm 0.10
Cadmium ^{a b c d}	75 \pm 7	Lead ^{a b d}	0.655 \pm .008
Chromium ^{b c}	403 \pm 12		
Copper ^{a b c}	609 \pm 27		
Nickel ^{a b d}	82 \pm 3		
Zinc ^{a b c d}	4760 \pm 140		
Uranium ^b	5.5 \pm 0.1		

^a. Atomic Absorption Spectrophotometry

^b. Isotope Dilution Mass Spectrometry

^c. Neutron Activation Analysis

^d. Polarography

^e. Spectrophotometry

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of J. K. Taylor.

The technical and support aspects involved in preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.

Washington, D.C. 20234
November 16, 1978

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

Preparation and Analysis

This SRM was prepared from urban particulate matter collected in the St. Louis, Missouri, area in a baghouse especially designed for this purpose. The material was collected over a period in excess of 12 months and, therefore, is a time-integrated sample. While not represented to be typical of the area in which it was collected, it is believed to typify the analytical problems of atmospheric samples obtained from industrialized urban areas.

The material was removed from the filter bags by a specially designed vacuum cleaner and combined into a single lot. This product was screened through a fine-mesh sieve to remove most of the fibers and other extraneous material from the bags. The sieved material was then thoroughly mixed in a V-blender, bottled, and sequentially numbered.

Randomly selected bottles were used for the analytical measurements. Each analyst examined at least 6 bottles, some of them measuring replicate samples from each bottle. No correlation was found between measured values and the bottling sequence. Also, the results of measurements of samples from different bottles were not significantly different than the measurements of replicate samples from single bottles. Accordingly, it is believed that all bottles of this SRM have the same composition.

The analytical methods employed were those in regular use at NBS for certification of Standard Reference Materials, except as noted in the following paragraphs. Measurements and calibrations were made to reduce random and systematic errors to no more than one percent, relative. The uncertainties of the certified values listed in the table include those associated both with measurement and material variability. They represent the 95 percent tolerance limits for an individual sub-sample, i.e., 95 percent of the sub-samples from a single unit of this SRM would be expected to have a composition within the indicated range of values 95 percent of the time.

The following values have not been certified because either they were not based on results of a reference method, or were not determined by two or more independent methods. They are included for information only. All values are in units of $\mu\text{g/g}$ of sample, unless otherwise indicated.

Aluminum	(3.3 wt. %)	Lanthanum	(42)
Antimony	(45)	Magnesium	(0.8 wt. %)
Barium	(737)	Manganese	(860)
Bromine	(500)	Potassium	(1.0 wt. %)
Cerium	(55)	Samarium	(4.4)
Cesium	(3)	Scandium	(7)
Chlorine	(0.45 wt. %)	Selenium	(24)
Cobalt	(18)	Silver	(6)
Europium	(0.8)	Sodium	(0.40 wt. %)
Hafnium	(4.4)	Thorium	(7.4)
Indium	(1.0)	Titanium	(0.40 wt. %)
Iodine	(20)	Tungsten	(4.8)
Vanadium	(130)		

The values listed below are based on measurements made in a single laboratory, and are given for information only. While no reason exists to suspect systematic bias in these numbers, no attempt was made to evaluate such bias attributable to either the method or the laboratory. The method used for each set of measurements is also listed. The uncertainties indicated are two times the standard deviation of the mean.

Nitrogen (NO ₃)	(1.07% ± 0.06)
Nitrogen (NH ₄)	(2.01% ± .08)
Sulfate	(15.42% ± .14)
SiO ₂	(26.8% ± .38)
Freon Soluble	(1.19% ± .47)

The above values were determined by the methods indicated below:

- Nitrate — Extraction with water and measurement by ASTM Method D992.
- Ammonia — NaOH addition followed by steam distillation and titration.
- Sulfate — Extraction with water and measurement by ASTM D516.
- SiO₂ — Solution and measurement by ASTM Method E350.
- Freon Soluble — Extraction with Freon 113, using the method described in "Standard Methods in Examination of Water and Waste Water," 14th Edition, p. 518, American Public Health Association, Washington, D.C.

J. W. Matwey supervised the collection of the material as well as sieving and bottling. The following members of the staff of the NBS Center for Analytical Chemistry performed the certification measurements: R. W. Burke; E. R. Deardorff; B. I. Diamondstone; L. P. Dunstan; M. S. Epstein; M. Gallorini; E. L. Garner; J. W. Gramlich; R. R. Greenberg; L. A. Machlan; E. J. Maienthal; and T. J. Murphy.

1 Development of an instrument to measure airborne sulfate
 particulate matter

Introduction

This progress report presents the results of further study of the pulsed flame photometric sulfur analyzer and of the effects of SO_2 and humidity on the calibration of the system with $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 aerosols. The system has been used in a mobile laboratory by the University of Minnesota in recent field studies and field calibration results will be compared with those obtained from laboratory calibration.

Calibration Results

The laboratory calibration technique consists of generation of an ammonium sulfate or sulfuric acid aerosol by atomization of the appropriate solution, followed by dilution with dry air and neutralization of the aerosol with a radioactive neutralizer. The humidity of the sample is adjusted by mixing with the required amount of moist air to give the desired relative humidity. Part of the sample is fed to the pulsed FPD system and part to an EAA (electrical aerosol analyzer) to determine the sample concentration.

Figure 12 shows the pulsed FPD system response to ammonium sulfate aerosols at various relative humidities with and without SO_2 added to the sample. Figures 13 and 14 show the response of the pulsed FPD system in mV output versus sample sulfur concentration in $\mu\text{gS}/\text{m}^3$ for ammonium sulfate and sulfuric acid, respectively. Calibrations were done at low humidification ($\sim 10\%$ r.h.) and at high humidification ($\sim 60\%$ r.h.) with SO_2 levels of 0 ppb and ~ 10 ppb.

The results in all figures show considerable scatter as well as a systematic dependence of the results on both SO_2 and relative

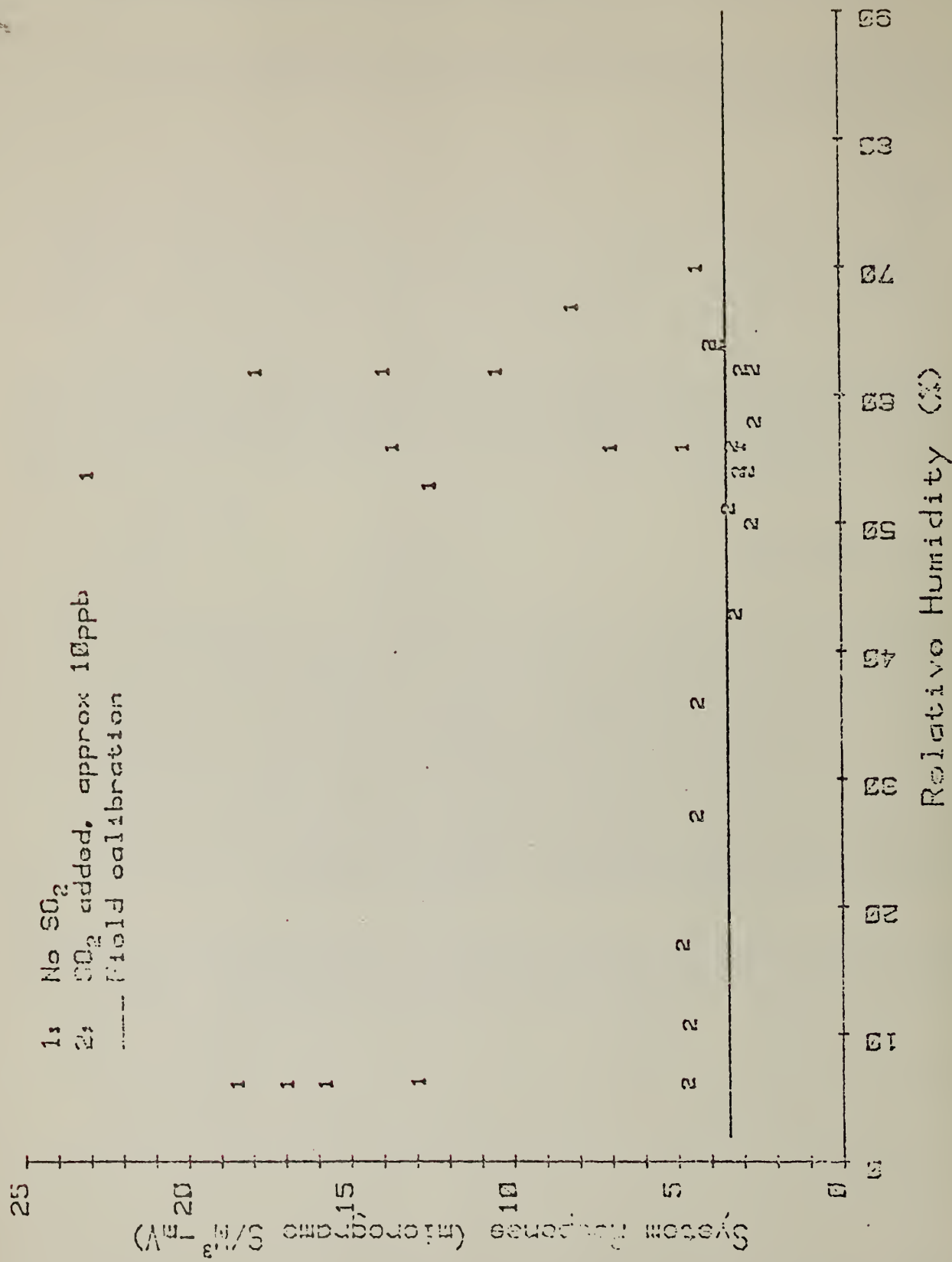
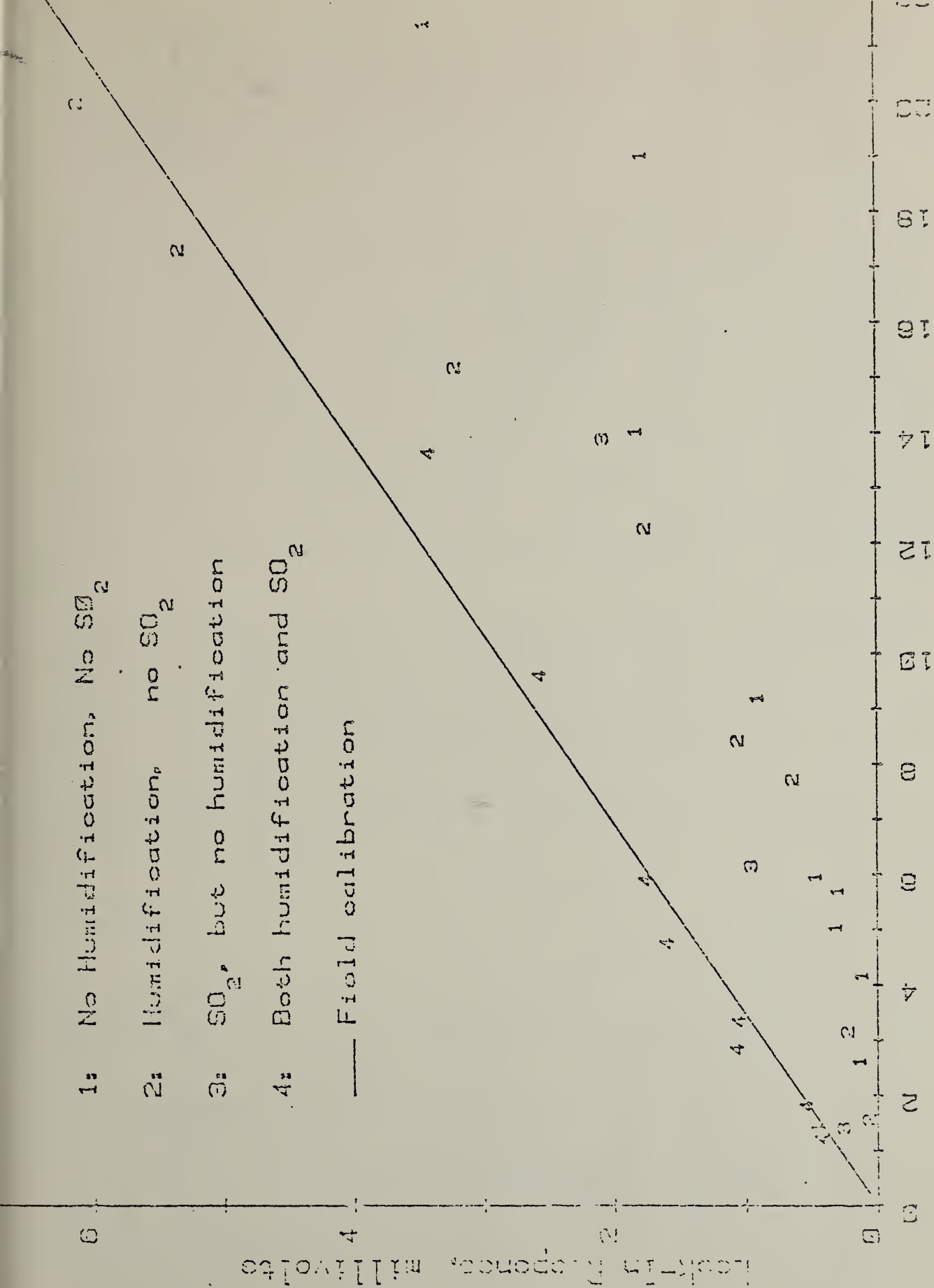


Figure 12. Pulsed FPD system response to ammonium sulfate aerosols at various relative humidities with and without SO₂ added to the sample.



Calculated Sulfur Concentration: micrograms/lit³
 Figure 13. Response of the pulsed FPD system in mV output versus sample sulfur concentration in µg S/m³ for ammonium sulfate.

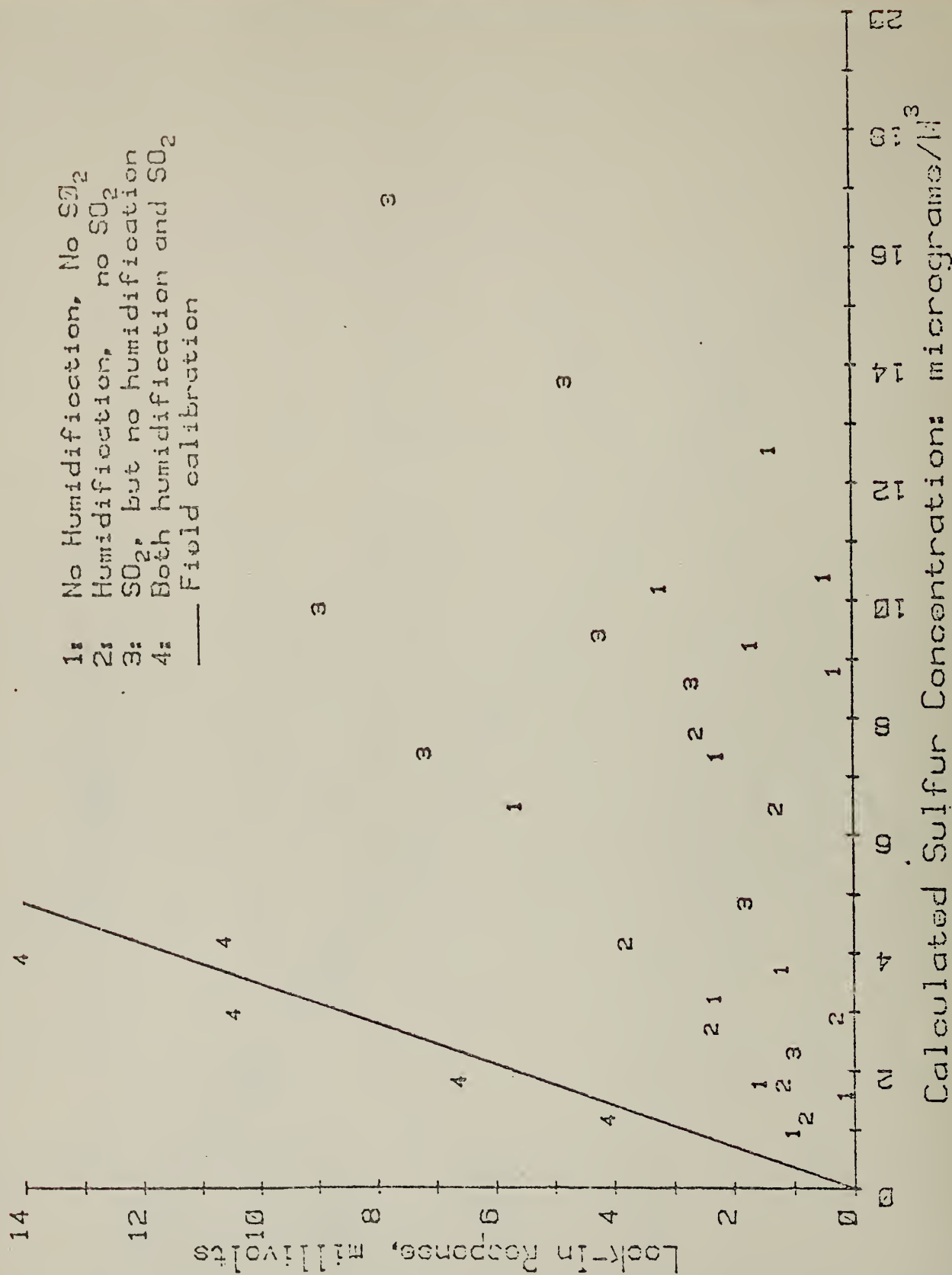


Figure 14. Response of the pulsed FPD system in mV output versus sample sulfur concentration in $\mu\text{g S}/\text{m}^3$ for sulfuric acid.

humidity. The results in Figure 12 showing instrument sensitivity ($\mu\text{gS}/\text{m}^3\text{mV}$) as a function of relative humidity are quite consistent in the presence of $\sim 10\text{ppb}$ added SO_2 , but show great scatter if no SO_2 is present.

In the figures a field calibration value is also indicated. This was obtained from a comparison of the average response of the sulfur monitor and x-ray fluorescence analysis of filter samples taken during the corresponding averaging time interval. This comparison gives a value of $3.45 \mu\text{gS}/\text{m}^3\text{mV}$ for the pulsed FPD instrument response. This is plotted in the figures and one can see that in the cases where the sample is humidified ($\sim 60\%$ r.h.) and where SO_2 is present ($\sim 10\text{ppb}$) the agreement with laboratory calibration results is quite good. This is encouraging because the field results were obtained under conditions similar to these.

We are still not able to explain the results for low relative humidity and SO_2 . Low SO_2 may accentuate some noise problems with the nonlinear amplifier in the FPD and signals around zero may cause problems in signal averaging by the lock-in amplifier. We are also going to check the use of the EAA as a means of characterizing the calibration samples by comparing it with values obtained by filter and QCM (quartz crystal mass monitor) measurements.

Conclusion

The pulsed-FPD sulfur analysis system has performed well in field study applications and the results obtained are in agreement with results obtained by other techniques. Several problems still exist related to the effect of relative humidity and gas phase sulfur on calibration techniques. We must determine if these effects are related to the system response or our calibration methods. Field and laboratory calibration values are consistent and in agreement for laboratory calibrations done under conditions similar to those in the field study.

80-BCL-c-ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

1 Radiocarbon as an Environmental Tracer

Introduction

The first results demonstrating the feasibility of mini-low level counting (*llc*) of radiocarbon to distinguish anthropogenic from natural pollutant sources, using only mg sample sizes, have been published (1,2). Following this accomplishment, we have taken steps to further extend our capabilities — in terms of sample size, throughput, and quality control. We have undertaken cooperative experiments at the request of the Oregon Graduate Center and the University of Washington to apply our unique method to two specific environmental problems. These particular applications served also as a logical next step in our research, for they allowed us to increase the discriminating power of the (*llc*) method through the addition of chemical and physical (particle size) selectivity.

Building on the experience of the past year, we are now developing future directions to make major advances in our capabilities through the use of accelerator mass spectrometry (AMS), large low-background proportional counters, stable isotope analysis, and trace gas radiocarbon analysis (Ref. 3 and App. III). These approaches will make possible far more selective and reliable information on source strengths, residence times and transport mechanisms of carbonaceous species in the environment; and the resultant data could provide important insight concerning paleopollution and the influence of atmospheric species on climate.

Parallel activities directed toward measurement accuracy and model validity have also taken place. A comprehensive treatment of the question of accuracy in chemical analysis has just been published

1(4), and a robust (assumption-resistant) approach to spectroscopic peak resolution will shortly appear(Appendix II)(5). This latter publication has important implications for the reliable extraction of pure component signals from overlapping peaks in chromatograms and X- and γ -ray spectra. An evaluation has just begun of high precision radiocarbon data from an international intercomparison involving 17 competent radiocarbon dating laboratories (this evaluation is indirectly related to the issuance of a new standard).

Quality Control and Measurement System Developments

As atmospheric species of interest exist at very low concentrations, we are attempting to a) improve our analytical technique by lowering detection limits to meet small sample size requirements (μg to mg), b) increase measurement precision for optimum source discrimination, and c) expand our multiple capability for increased throughput. For samples at the 5-10 mg carbon level, we are currently striving to improve (11c) precision from the existing 10 percent to 1-3 percent*, by assuring an adequate level of quality control and by improving counter design. Through β counting of natural radiocarbon is only practical for as little as 1 mg of carbon (restricted by Poisson Statistics), the accelerator technique (AMS) for carbon-14 counting holds the only prospect of reaching the μg level for environmental and dating problems with good precision. Because of the complementary nature of the two approaches, we are currently investigating both.

*In Ref. 2 [Eq. 1,2] we showed that a relative standard deviation of three percent could be achieved in principle, simply by extending our counting period to one week.

Quality control for the existing (11c) system (at the 5-10 mg carbon level) is presently taking place through the replication of background and standard measurements. Background measurements which are monitored between sample and standard counts, utilize CO₂ from dry ice, P10 (90% Ar and 10% CH₄), and CH₄, all of which are derived from natural gas. Also used is a blank standard, sub-bituminous coal - SRM 1635. Table 18 summarized background measurements for newly constructed 5 and 15 mL counters.

TABLE 18

Counter Backgrounds

Counter (nominal volume)	Counting Gas	Source	Count Rate ^a (cpm)
N ^b (5 mL)	CH ₄ - 3.7 atm	Natural Gas	0.081 ± 0.008
	CO ₂ - 3.9 atm	Natural Gas	0.093 ± 0.009
	CO ₂ - 2.8 atm	Sub-bituminous Coal - SRM 1632a	0.087 ± 0.005
J ^c (5 mL)	CO ₂ - 4.2 atm	Natural Gas	0.094 ± 0.004
M ^c (15 mL)	CO ₂ - 1.0 atm	Natural Gas	0.132 ± 0.008

^aUncertainties represent Poisson standard deviations.

^bExternal iron shielding.

^cExternal lead shielding.

Beyond the limit of our shielding, i.e., thick iron or lead external shielding plus pure copper internal shielding, the background rate is limited by counter size and construction material purity. In order to minimize these effects, counters have been constructed of high purity quartz, and volume has been reduced such that elevated pressures are required to assure sufficient sample activity. These experiments have been successful in that routine operation up to several atmospheres is not possible, with no detectable pressure dependence of the background rate. The international radiocarbon dating standard (Oxalic Acid, SRM 4990B) has been used for counter calibration, and this and two other reference samples have been used for quality control or inter-laboratory comparison of percent contemporary carbon activity of environmental samples. The following materials are used in our laboratory: NBS contemporary oxalic acid, SRM 4990B; USGS wood sample (7060 ± 250 yrs. B.P.); and urban dust air particulate, NBS SRM 1648 (Table 19).

The results in Table 13 thus illustrate three phases of our work: calibration (NBS-Oxalic Acid SRM-standard), measurement (urban dust SRM), and quality control (USGS wood sample). The result for the USGS wood (counter N) is consistent with the known age, and the result for the urban dust is the first quantitative radiocarbon assay of that material.

Quality control for (11c) is monitored by a continuous record of anticoincident count rate, meson rate, and guard rate. Figure 15 is an illustration representing data from our measurements of the USGS wood sample. The parameters monitored (R_G , R_U , R_{AC}) permit us to assess electronic and counter stability, meson cancellation efficiency, and counting gas purity. A fourth parameter, barometric pressure, will be added for high precision measurements and evaluation of trends in guard and meson rates. For the initial observations (1-4) in figure 15, neither precision nor control

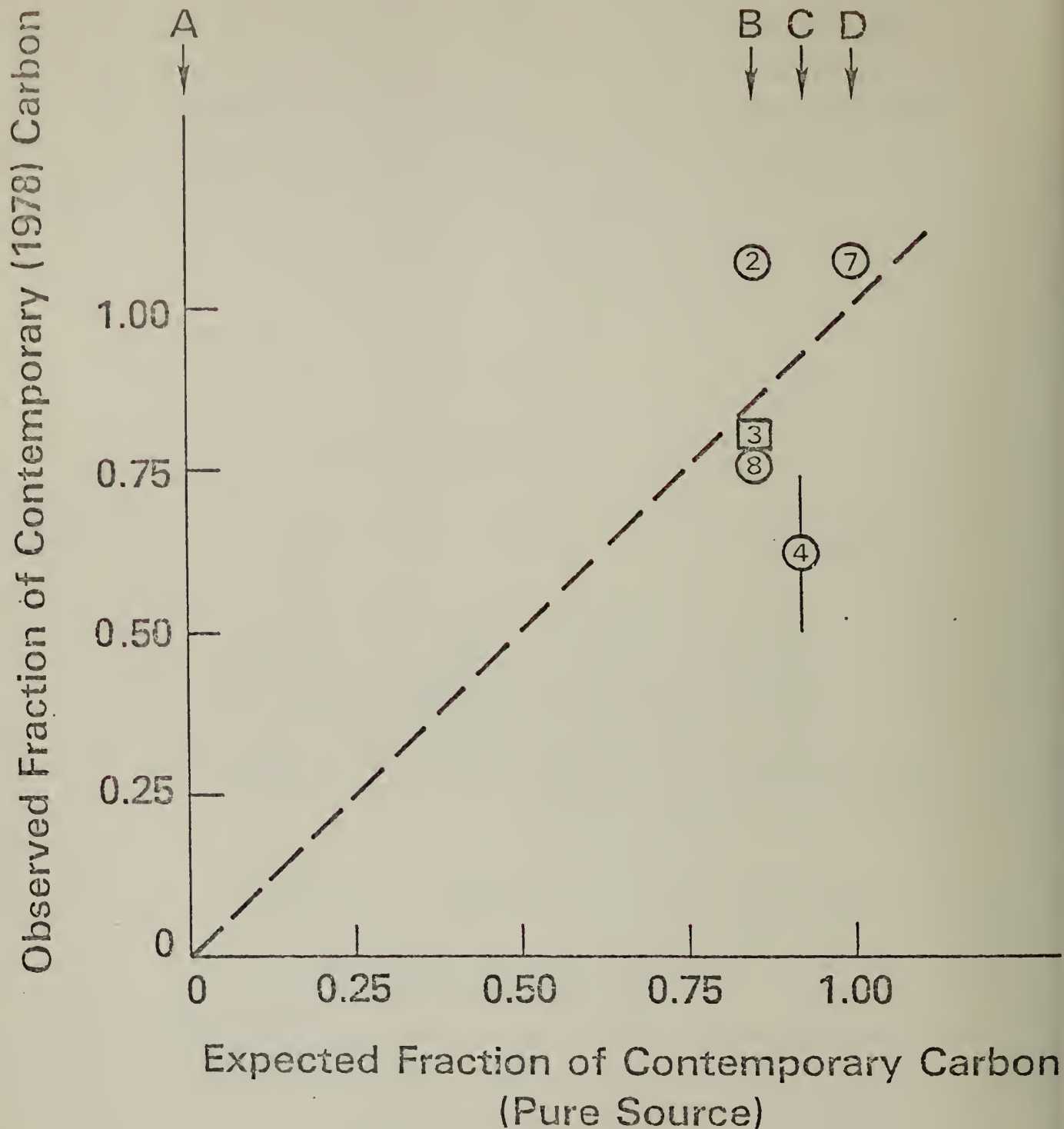


Figure 15. Anticoincident (R_{AC}), meson (R_u), and guard (R_G) count rates (cpm) versus run number for USGS Wood Sample utilizing Counter J. Poisson uncertainties ($\pm 1\sigma$) are represented by error bars for corresponding point symbols.

TABLE 19

Standards and Reference Samples

Counter (nominal volume)	Counting Gas	Standard and Reference Samples	Net Count Rate (cpm/10 mg C) ^a	Percent Modern ^b Carbon
N	CO ₂	NBS - Oxalic Acid SRM 4990B	0.090 ± 0.005	105%
		USGS Wood Sample (7060 ± 250 yr B.P.)	0.029 ± 0.005	34%
		NBS - Urban Dust SRM 1648	0.048 ± 0.006	56%
J (5 mL)	CO ₂	NBS - Oxalic Acid SRM 4990B	0.097 ± 0.007	105%
		USGS Wood Sample (7060 ± 250 yr B.P.)	0.038 ± 0.004	41%
M (15 mL)	CO ₂	NBS - Oxalic Acid	0.085 ± 0.009	105%

^aUncertainties represent Poisson standard deviations.

^bPercent modern carbon = $\frac{\text{Net Sample Activity}}{0.95 \times \text{NBS Oxalic Acid SRM}} \times 100\%$.

were adequate, due in part to insufficient counting time and external difficulties (air conditioning and computer shutdown). For the rest of the sequence, all observations are consistent with counting statistics, except for small barometric pressure related variations in R_G and R_μ .

A planned expansion of our multiple counter capability is under-way (—first) through the investigation of source(s) of spurious pulses. Our present system, which uses two-dimensional spectrometry, (energy vs rise time), is limited to the simultaneous

operation of four counting channels. If sources of spurious pulses can be identified and controlled, then counting can be accomplished by energy discrimination only. It would be then much more practicable to utilize the full capacity of our present shielding, which can accommodate 50 to 100 counters. A Cromemco Z-2 Computer System, with an 8-inch dual floppy-disc drive, line printer, viewing screen, and teletype will be installed shortly (J. R. DeVoe, personal communication) for acquisition and reduction of radiocarbon data. With this new system environmental parameters influencing count rate, such as barometric pressure, room temperature, and humidity, as well as the previously discussed counter-control parameters, can be continuously monitored.

Applications to Pollutant Source Identification

During the past three months experiments have been completed to access the applicability of radiocarbon measurements (22c) to resolve the contributions of field and slash burning, wood stoves, natural emissions, fossil fuel combustion, etc. to the total urban particle load in areas such as Portland and Eugene, Oregon (6). This cooperative project with Prof. John A. Cooper of the Oregon Graduate Center (OGC) complements an extensive analytical program at OGC to determine the major sources of airborne carbonaceous and non-carbonaceous particles. From the many particulate samples taken in the Portland area at different locations, and for differing collecting periods, meteorological conditions, and particle size fractions, a select group (filters #1-8, see Table 20) was taken for radiocarbon assay as most representative of the sources in question. Radiocarbon results will later be compared to the results of inorganic analyses to develop a powerful tool to derive quantitative information on sources of fine particles as an aid in defining sources on days when air quality criteria are exceeded.

TABLE 20

Modern Carbon in Portland Aerosols

Filter Number	Collection Date	Primary Impact	Size Fraction	Carbon	
				Mass (mg)	Percent Contemporary
1	18 Oct. 77	Slash	Total	48	47 \pm 12
2			Fine	11	107 \pm 18
3			Fine	21	80 \pm 15
4	23 Jan. 78	Fireplace	Fine	24	62 \pm 13
5			Total	72	45 \pm 12
6	17 Aug. 77	Violation (No Burning)	Total	22	77 \pm 15
7	11 Aug. 78	Field	Fine	42	107 \pm 15
8	3 Aug. 78	Slash	Fine	29	76 \pm 12
Total				72	104 \pm 16

As with our previous study (1), the Oregon aerosol project utilized radiocarbon (^{14}C) for source discrimination. Two new elements are added, however: a) not all of the Oregon sources can be distinguished with ^{14}C (vegetation contains modern carbon), and b) selectivity was enhanced through the measurement of radiocarbon in size-fractionated material. Further discussion of these matters will be found in References 3 and 6; and a visual summary is given in figure 16, which shows that the radiocarbon content of the fine particle fraction is a reliable indicator for sources such as field, slash, and fireplaces.

A second cooperative study (with J. Swanson, Univ. Washington) relates to the organic fraction in marine sediments, which is derived primarily from planktonic matter. Of this fraction, the

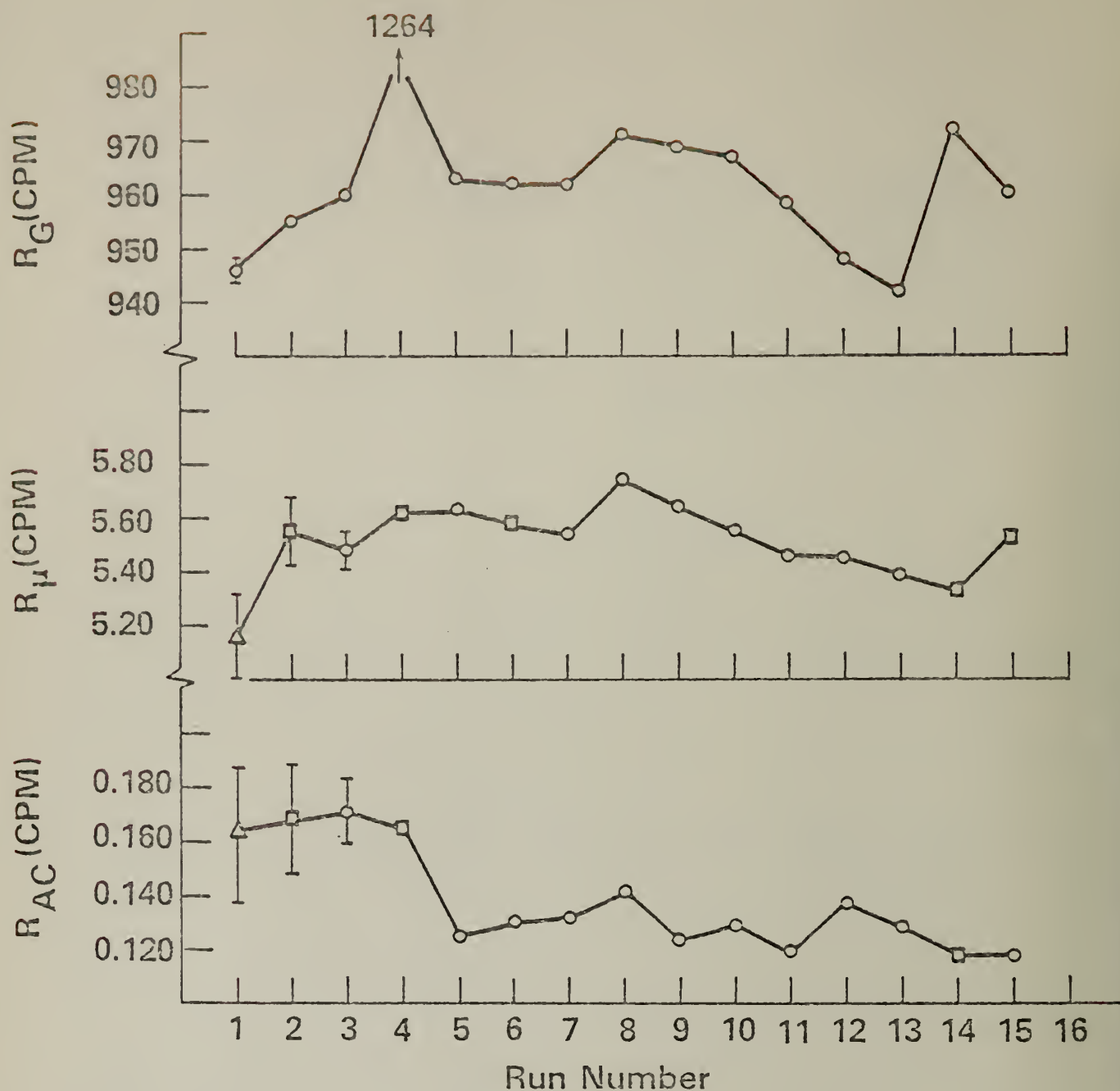


Figure 16. Comparison of observed with expected vegetative impact (fine particles). Dashed line represents the idealized situation for a pure source. The numbered box (15) indicates the median result; and the individual result uncertainty ($\pm 1\sigma$) is shown for sample #4 only, for clarity. Abscissa locations (A,B,C,D) are derived from the atmospheric radiocarbon input function and the mean ages (t) of the material burned. A (fossil fuel, $t \gg ^{14}\text{C}-t_0$), B (slash, t at core ~ 200 yrs.), C (fireplace, t at core ~ 40 yrs.), D (field, $t \sim 0$).

lipid component constitutes 20 to 50 percent, and 5 to 20 percent of this is in the form of fatty acids with the remainder being hydrocarbons. Polycyclic aromatic hydrocarbons (PAH), known to include carcinogens, have been extracted from the lipid fraction. Since there is some question as to whether a natural marine source for PAH exists, it was suggested (Swanson, personal communication) that measurement of the radiocarbon content of the aromatic and fatty acid fractions could help identify the source. Presently there are contradictory opinions as to the major source of PAH found in marine sediments. Blumer et al., (7), have investigated the molecular weight distribution of the PAH in marine sediments from Buzzards Bay, Massachusetts. They found the unsubstituted hydrocarbons predominate and suggest that (natural) forest fires form, and that air currents disperse, a complex PAH assemblage that eventually accumulates in soils and recent sediments.

On the other hand, Hites et al. (8), found a correlation between the time distribution of alkyl homologs of PAH in sediment, and the timed distribution calculated for coal, wood, oil, hydro-electric, and gas combustion-product PAH. The authors specifically suggested that fossil fuel combustion is the primary source of PAH in recent (1850-present) Buzzard Bay, Massachusetts marine sediments. The objective of our cooperative project with Swanson will therefore be to test the hypotheses that the PAH fraction is primarily natural or anthropogenic in origin. Our (77c) system is required because it is quite impractical to get more than 10-20 mg of aromatic hydrocarbons from large amounts of sediment.

A third environmental matter to which we are now giving major attention is the question of the relative amounts of atmospheric CH_4 , CO , and light hydrocarbons that are generated by man compared to that from natural sources. Previous investigations (9,10) of the radiocarbon in atmospheric CH_4 showed the average contemporary carbon content as 80 percent, indicating that four-fifths of the

CH₄ was of recent biological origin. Atmospheric carbon monoxide was also investigated (11), and found to be 75 percent contemporary carbon. These data are questionable, however, since the samples were provided by air-liquefaction plants situated in industrial areas. Our current plans therefore call for remeasuring ¹⁴C in these gases in contamination-free regions using portable sampling apparatus.

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Appendix 1

Resolution of Spectral Peaks: Use of Empirical Peak Shape*

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ABSTRACT

A semiempirical method of gamma-spectrum peak resolution (PICO), which uses experimentally determined singlet peak shapes, has been devised to minimize sensitivity to systematic deviations from assumed analytic shape functions. The resolving power and accuracy of the method have been demonstrated through the use of International Atomic Energy Agency test spectra having Poisson measurement precision of about 0.5 percent and peak separations ranging from approximately 0.3 to 1.3 full width at half maximum.

* Proc. Conference of Computers in Neutron Activation Analysis and Gamma-Ray Spectroscopy (American Nuclear Society, in press).

ADVANCES IN THE DISCRIMINATION OF NATURAL FROM ANTHROPOGENIC
CARBONACEOUS POLLUTANTS VIA ISOTOPES OF CARBON

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Introduction

Alteration of the natural radiocarbon concentration in living matter by the dilution of atmospheric carbon dioxide with fossil ("dead") carbon was first recognized by Suess (1) through the examination of the $^{14}\text{C}/^{12}\text{C}$ ratio in early twentieth century tree rings. This dilution effect was subsequently employed by Clayton et.al. (2) and Lodge et.al. (3) to estimate the anthropogenic (fossil carbon) contribution to carbonaceous atmospheric particulates in urban locales. Although the potential of this method for determining the impact of man's use of fossil fuels on the current and historical burdens of carbonaceous pollutants was clear, its application was severely limited by the large samples required -- typically grams of carbon -- for measurement with conventional radiocarbon dating facilities. The possibility of overcoming the foregoing limitation through the use of miniature, high-purity, low-level counters was investigated two years ago (4); and the first measurements on milligram amounts of carbon from air particulate samples were reported earlier this year (5).

Measurement Techniques; Results

Two approaches currently exist for the assay of the radiocarbon content of atmospheric carbonaceous gases and particles, using small (~mg) carbon samples: mini-low level counting (llc) and Accelerator Mass Spectrometry (AMS). Both methods are appropriate for the resolution of fossil from biogenic carbon in environmental pollutants. The advantage of llc is that it is already developed for routine use and it requires somewhat less expensive facilities; AMS has the potential for greater throughput and improved precision. A comparison of the Poisson precision of the two methods applied to environmental samples is given in the proceedings of the first Conference on the new accelerator technique (6). Recent developments in our llc method, involving multiple counting channels and improved detector design, give us the possibility of achieving adequate pollutant source discrimination with a throughput of about one result every three hours (10mg - C).

The 11c approach is currently being applied to milligram samples of atmospheric gases (CH_4 , CO), urban and rural particulate material, and natural and pollutant organic species in marine sediment (7). Details of the sampling, preparation of high purity CO_2 counting gas, and special counting techniques have been given in Ref. 5. Requisite counting sensitivity was achieved through the design of small volume (5-15 mL) high purity quartz proportional counters with minimal dead volume, and through the combination of pulse energy and pulse shape analysis to discriminate against radioactive contaminants and electronic noise. These measures led originally to a net signal from 10 mg of contemporary carbon which was comparable to the background rate, both being about 0.1 cpm. As a result, an adequate level of (Poisson) precision could be achieved with about a one day count. Results of 11c applied to urban and desert samples (5) showed over 70 percent fossil carbon in the urban samples, but little if any in the desert sample. The smallest sample size in the set consisted of just 5.3 mg-C; this sample, collected in Salt Lake City, yielded a result of 72 ± 13 percent fossil carbon in 2.7 days of counting time.

Future Directions: Chemical and Isotopic Selectivity

The dichotomous "dead or alive" hypothesis for distinguishing anthropogenic from natural carbonaceous pollutants is too simple. Though useful when the two source components are chemically stable and strictly correlated with fossil and biogenic (living) carbon, the hypothesis breaks down in certain cases involving contaminable/unstable sample species or when non-fossil carbon is released through man's activities (or the converse). Fossil carbon, for example, can be released through natural volcanic or geothermal activity; and biogenic carbon can be released through man's burning of wood, fields, etc. Similarly, radiocarbon itself arises from both natural (cosmic ray interactions) and anthropogenic (nuclear tests, reactors, tracer experiments) sources.

In order to achieve reliable conclusions with such a multiplicity of sources, we can: (a) employ carefully-designed sampling plans, (b) augment the radiocarbon measurements through the selection of critical particle sizes and chemical species, and (c) add a second dimension to our isotopic space through the measurement of ^{13}C . The first two approaches have already been implemented (7), and the third is under investigation. Typical of the sample selection referred to is the separation of size fractions for the removal of large biogenic particles (spores, etc.), and the measurement of radiocarbon in individual chemical fractions such as "soot", and aliphatic and aromatic hydrocarbons.

Table 1
ISOTOPIC SOURCE INDICATORS

^{14}C (%) (a)			^{13}C (%) (b)		
	<u>Concentration</u>	<u>Variation</u>		<u>Concentration</u>	<u>Variation</u>
artificial ^{14}C	>> 100.	unpredictable	PDB (CO_3)	0.	---
biosphere	~ 130.	injections, dispersion	CO_2 (atm)	-0.7	sl. seasonal, local effects
cosmic rays	100.	solar, geomagnetic field	C_4 plants (grasses)	-10 to -18	species, local climate
decay	$\tau = 8270$ yr.	---	C_3 plants (trees), coal, petroleum	-22 to -32	species, local climate, precursors
fossil fuel	0.	---	Natural gas	-35 to -48	species, precursors
			Dry ice	-52	

(a) Standard (100%) is 0.95 x NBS oxalic acid SRM. See references 8 and 10, for causes and magnitudes of variation.

(b) Standard (0%) is Peedee Belemnite. (Conventional units are ‰.) See reference 9 for information on standard and variations.

By complementing the radioisotope (^{14}C) measurements with information on the stable isotopic (^{13}C) composition, we have the possibility of increased source resolving power. As shown in Table 1, the ability to resolve fossil carbon from most living plants lies with ^{14}C , whereas ^{13}C provides the means to resolve certain classes of fossil fuels as well as certain classes of living matter (C_3 from C_4 plants). Two important conclusions regarding the use of the carbon isotopes are apparent from the table: (a) careful attention must be paid to the causes and ranges of intraclass variations, and (b) the concentration differences between (resolvable) sources imply the requisite measurement accuracy. That is, an uncertainty of about 10% is adequate for ^{14}C , but as little as 0.1% is required for ^{13}C measurements.

In conclusion, a brief survey will be given of some environmental problems which may be attacked with the new approaches. These include: the identification of fossil, natural and nuclear (power, testing) sources of atmospheric carbon; the assay of pathways and residence times for atmospheric carbonaceous species; and the investigation of the historical record of carbonaceous sources via analysis of material from ice cores and sediment.

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- ⁷Radiocarbon measurements on small samples (mg-carbon) have been applied to assess urban carbonaceous pollution from fossil sources (Reference 5) and vegetative sources (J. A. Cooper, L. A. Currie, and G. A. Klouda, to be published), and to define the anthropogenic component in marine sediments (J. Swanson, A. Fairhall, and L. A. Currie, to be published).
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SO-BCMa-ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING
AND ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

1 Energy Related Water Pollutant Standard Reference Materials

1.a Complete Certification of Ocean Sediment SRM

No activity in this project during the past six-month period.

1.b.i Estuarine Sediment, Proposed SRM 1646

The material for Proposed SRM 1646, Estuarine Sediment was collected by personnel of the Virginia Institute of Marine Sciences at coordinates 37 11.1 N, 76 17.1 W in the Chesapeake Bay. The material was freeze-dried and irradiated at 2.5 megarads.

At NBS, the material was sieved through an 18 mesh sieve to remove coarse contaminants, and then ball-milled to pass a 100 mesh sieve. The sieved material was blended for 45 minutes. As anticipated, the chemical composition of Proposed SRM 1646 is significantly different from SRM 1645, River Sediment. At present, Proposed SRM 1646 is being analyzed by neutron activation analysis to determine the inhomogeneity of the 150 kg of processed material. (See Appendix IV for certification of SRM 1645).

1.b.ii Preconcentration and Separation of Sea Water Transition Elements

A comprehensive report entitled, "The Quantitative Removal of the Alkali and Alkaline Earth Elements from the Trace Transition Elements in Sea Water Using Chelating Resin, and Its Application to Analytical Instrumental Techniques," has been completed and will be submitted to EPA for publication as an EPA Technical Report.

1.c Anions in Water SRM

No activity in this project during the past six-month period.

1.d Anion SRM

No activity in this project during the past six-month period.

1.e Anion and Trace Elements in Water SRM

SRM 1643, Trace elements in water, has been completely sold out. The certification of a much larger trace element in water SRM is now in progress.

1.f The Role of Internal Standardization in Analysis of Aqueous Samples Using the Inductively Coupled Plasma (ICP) Technique

As indicated in the previous report, the application of the ICP technique to water analysis requires instrumental background correction. This need arises because of background shifts between samples and standards which introduce systematic error. Spectral scanning was shown to be an effective approach to this measurement problem. However, since the total analysis time is lengthened, the possibility of instrumental drift is increased. Preliminary data has indicated that when such drift does occur, it is due to variability of nebulizer aspiration. Under these conditions similar behavior has been noted for groups of detector channels in the direct reading spectrometer. Ratios of appropriate channel pairs should, therefore, exhibit significantly less drift, indicating the feasibility of internal standardization.

An operational rather than theoretical approach was chosen which would examine the statistical behavior of all possible channel-to-channel ratios during a normal analysis time period (40 min.). Raw intensity data for three multi-element solutions were reduced

by the NBS central computer to evaluate all possible intensity ratios. These ratios as well as the raw intensities were then statistically analyzed for random and normally distributed variability [1]. Intensity ratios which exhibited significant improvement in relative standard deviation (RSD) were grouped as possible internal standard elements. Seven elements were then ratioed to the best internal standard for each, and the degree of RSD improvement over the raw intensity data was examined at various signal to background ratios. The results are plotted in Figure 17. The plot indicates that with proper choice of an internal standard, the variability of response can be improved upon by at least a factor of two, if the signal-to-background ratio for the analyte element is ten or greater. Under such conditions it has also been found that long-term (6 hrs) drift of intensity ratios is limited to less than one percent while the raw intensity drift was five percent. Frequency of restandardization can thus be reduced for routine analyses utilizing internal standardization.

Future developments will involve the application of new spectrometer and computer systems which will allow photographic as well as electronic multi-channel detection of ICP emission. In the multi-channel mode complete flexibility as to line choice, observation height and automatic scanning background correction will be available. Furthermore, spectral resolution will be a factor of ten better than the present direct reading spectrometer allowing more complete separation of analyte emission lines from those of the matrix.

Reference

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EFFECT OF I.S. ON R.S.D.

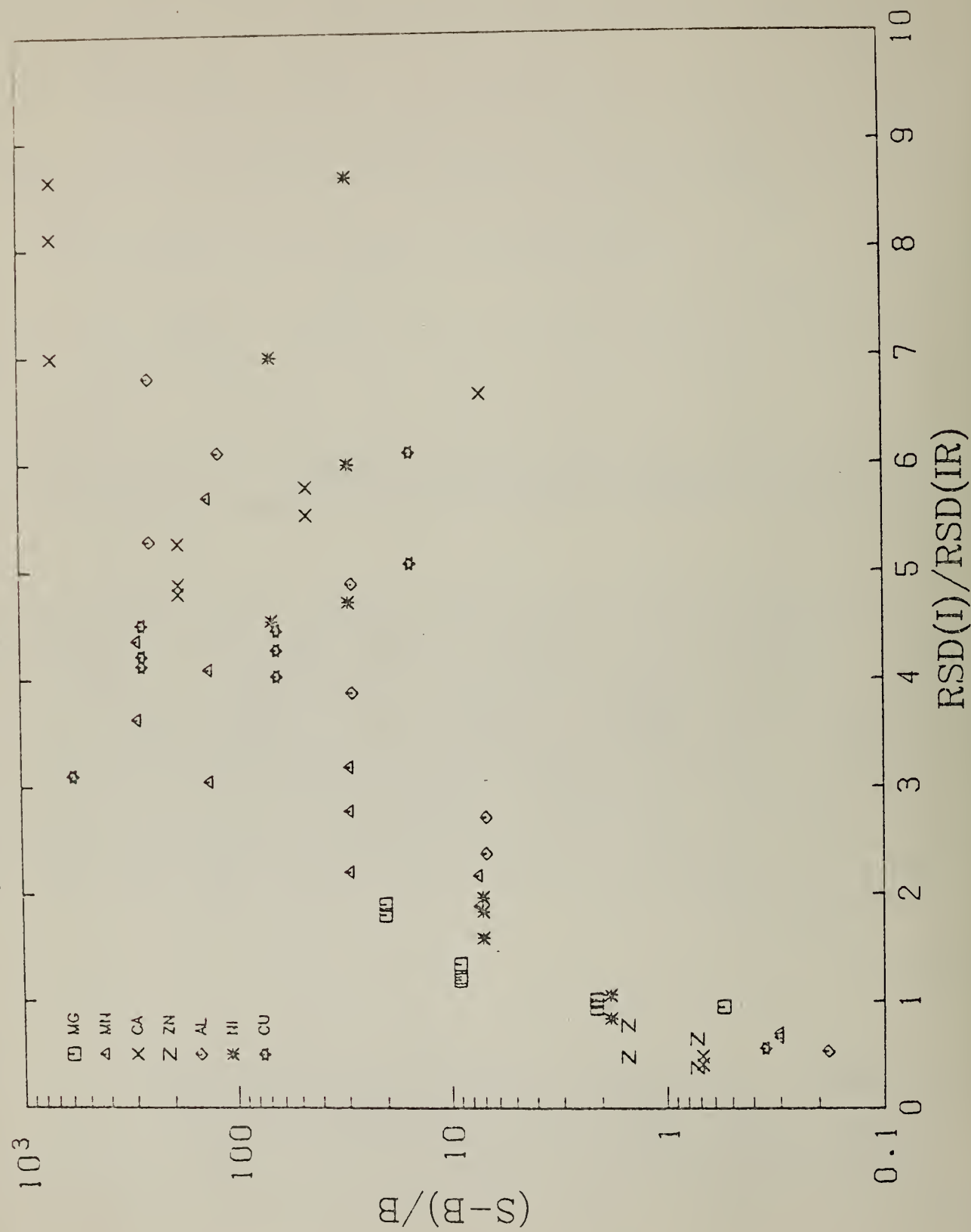


Figure 17. Degree of RSD improvement over raw intensity data examined at various signal to background ratios for seven elements

2.a/b Production of an Aqueous PAH SRM

Research on the feasibility of using PAH generator columns as SRMs for PAH in water has been completed. We are now in the procurement process for the production of this material. A copy of the request for bid submitted to the Department of Commerce is appended to this report (Appendix V).

Direct Injector for a Capillary Gas Chromatograph Used in Air and Water Pollution Analysis

Normal injection techniques for capillary gas chromatography preclude the introduction of more than 100 nL (10^{-7} L) onto the chromatographic column. It is necessary, however, for trace analysis of environmental materials to place a considerably greater volume of sample (1 to 5 μ L) onto the column in order to be able to detect some of the low level organic compounds contained in the sample. A number of special splitless injection techniques (such as that developed by Grob and Grob) have been developed in order to allow large sample volumes to be placed on the chromatographic column without undue loss of system resolution. These splitless methods have been shown (Table 21) to yield systematic losses for solutes with boiling points approximately 50 °C in excess of the injector temperatures. Thus, since the maximum injector temperature is 350 °C, losses might be expected for any analytes with boiling points greater than 400 °C. The boiling points of some polynuclear aromatic hydrocarbons (PAHs) which can be successfully eluted without on column losses are listed in Table 22. If the compounds containing four or more rings are to be accurately determined by gas chromatographic means, a new method of sample injection will have to be used.

TABLE 21

Comparison of Normal and Splitless Injector Techniques
Injector Temperature 350 °C

<u>Compound</u>	<u>Boiling Pt °C</u>	<u>Peak Area Splitless^a</u> <u>Peak Area Normal</u>
5-methyl tetradecane	264	1.3
n-hexadecane	287	1.3
n-eicosane	343	1.5
n-tetracosane	341	1.2
squalane	350	0.8
n-hexacosane	414	0.8
n-octacosane	440	0.5

^a If both injector techniques are temperature independent, the ratio should remain constant.

TABLE 22

Boiling Points of Some Polynuclear
Aromatic Hydrocarbons

<u>Compound</u>	<u>Boiling Pt</u>	<u>Number</u> <u>of Rings</u>
napthalene	210 °C	2
phenanthrene	340 °C	3
1,2,benzanthracene	435 °C	4
chrysene	448 °C	4
benz(a)pyrene	>450 °C	5
coronene	525 °C	7

A direct injector is being developed at NBS which places a liquid sample, of between 1 and 10 μ L, on the head of the capillary column, completely bypassing the normal heated injection port. This injector consists of a pressurized glass tube in which the head of the capillary column is placed and immobilized and a steel rod in which a sample cup has been inserted. This steel rod slides through a pressure sealing O-ring down the glass tube until the head of the capillary column just touches the bottom of the sample cup. The liquid sample, which had previously been placed in the cup with a microliter syringe, is transferred to the column by capillary action. This injector has been shown not to adversely affect chromatographic resolution and preliminary experiments indicate that the injector is boiling point independent.

2.c Development of a Phenols-in-Water SRM

In some of our earlier reports we have presented preliminary results of a study of the stability of some selected phenols in distilled water. That study has now been completed and the final results are given in Table 23. The data show that the concentrations of phenol, o-cresol, and p-cresol remained constant throughout the 27 month study. The concentrations of 2-naphthol and 2,4,6-trimethylphenol decreased with time. The concentration of each of these five compounds in a 10 percent benzene/90 percent hexane solution was constant throughout the 27 month period.

We have previously stated that the two most probable causes of these losses were adsorptive losses to the walls of the glass ampoules and biodegradation. Of these two probable causes, the former seems to be the most probable cause for the observed phenomenon. The two compounds that were lost from solution were the least water soluble and most likely ones to adsorb on and cling to the walls of the ampoules. On the other hand there is no reason to assume that both 2-naphthol and 2,4,6-trimethylphenol would be more susceptible to biodegradation than phenol or the two cresols.

TABLE 23

Stability of Selected Phenols in Distilled Water

Compound	Gravimetric Concentration Added (mg/L.)	b					c			
		Day 1	Day 92	Day 175	Day 491	Day 608	Day 804			
phenol	21.0	19.9 ± 0.4	22.2 ± 1.1	21.7 ± 0.5	21.0 ± 0.4	20.5 ± 0.3	20.8 ± 0.6			
<i>p</i> -cresol	54.3	53.9 ± 0.2	57.2 ± 1.2	55.0 ± 0.8	54.6 ± 1.3	52.8 ± 0.7	54.0 ± 1.6			
<i>o</i> -cresol	34.3	35.3 ± 0.4	37.6 ± 1.1	34.5 ± 0.9	33.5 ± 0.9	32.5 ± 0.5	33.1 ± 0.7			
2-naphthol	71.4	71.4 ± 0.4	70.6 ± 0.9	69.5 ± 0.7	67.1 ± 0.7	67.6 ± 0.9	68.8 ± 3.4			
2,4,6-trimethyl- phenol	38.3	38.8 ± 0.7	39.3 ± 3.3	35.4 ± 3.6	34.3 ± 0.3	33.8 ± 1.3	33.1 ± 3.9			

^aConcentrations measured by high performance liquid chromatography.^bResults represent the combined average obtained from triplicate analysis of five ampoules.^cResults represent the combined average obtained from triplicate analysis of two ampoules.

We also have concluded that radiation sterilization is not a practical means of quenching any biological activity that might occur in such solutions. The data given in Table 24 shows that an irradiation dose of 1.5 megarads (suggested by D. Woodward, Neutron Products Inc., Dickerson, Maryland) causes molecular degradation within the solution.

Given this information, we have decided to initiate a similar study using a coal by-product water, where we have added 1-100 ppm of the same five compounds plus several other hydroxylated aromatics. The purpose of this study will be to determine whether the highly water soluble compounds again show a high degree of stability and if the increased organic content of this matrix will enhance the stability of less soluble compounds such as 2-naphthol and 2,4,6-trimethylphenol and some hydroxylated PAHs.

2.d Development of SRMs for Organics in Sediment and Biota

More data on the Muscle Intercomparison Exercise are being compiled, and the compilation should be available for the next semi-annual report.

2.e Spectroscopic Certification Technique for Analysis of Trace Organics in Water SRM

No activity in this project during this six-month reporting period.

TABLE 24

Degradation of Aqueous Solutions of Phenols Due to
Radiation Treatment^a

Compound	Gravimetric Concentration Added (mg/l.)	Concentration Found (No Radi- ation Treatment) (mg/L)	Concentration Found (Post radi- ation Treatment) (mg/L)	Loss Due to Radiation Treatment (%)
phenol	21.0	20.5	8.4	59
<i>p</i> -cresol	54.3	52.8	13.7	74
<i>o</i> -cresol	34.3	33.1	10.3	69
2-naphthol	71.4	68.8	2.2	97
2,4,6-trimethyl- phenol	38.8	33.1	2.3	93

^a Irradiation Dose, 2.5 megarads.

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 1645

River Sediment

This Standard Reference Material is intended for use in the calibration of methods used in the analysis of river sediment and materials with similar matrices. The material has been freeze dried and is now essentially free from moisture. The certified values given below are based on measurements made on a dried sample of at least 100 mg for the trace elements and for a 1-g sample for iron and chromium.

The values are based on the results of 6 to 30 determinations by the analytical techniques indicated. The estimated uncertainties include those due to sample variation, possible method differences, and errors of measurement (see Preparation and Analysis).

Element	$\mu\text{g/g}$	Element	$\mu\text{g/g}$
Cadmium ^{c d}	10.2 \pm 1.5	Thorium ^b	1.62 \pm 0.22
Copper ^{b c}	109 \pm 19	Uranium ^b	1.11 \pm .05
Lead ^{b d}	714 \pm 28	Vanadium ^{a c}	23.5 \pm 6.9
Manganese ^{b c}	785 \pm 97	Zinc ^{a d}	1720 \pm 169
Mercury ^{a c}	1.1 \pm 0.5		<u>Weight %</u>
Nickel ^{b d}	45.8 \pm 2.9	Chromium ^{b c}	2.96 \pm 0.28
Thallium ^b	1.44 \pm 0.07	Iron ^{a c}	11.3 \pm 1.2

^a Atomic Absorption Spectrometry

^b Isotope Dilution Mass Spectrometry

^c Neutron Activation Analysis

^d Polarography

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of J. K. Taylor.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.

Washington, D.C. 20234
November 16, 1978

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

Instructions for Use

The material, as received, is essentially free from moisture. In case of exposure to moisture, it should be dried without heat to a constant weight before using. Recommended procedures for drying are: (1) drying for 24 hours using a cold trap at or below -50°C and a pressure not greater than 30 Pa (0.2 mm Hg); (2) drying in a desiccator over P_2O_5 or $\text{Mg}(\text{ClO}_4)_2$. When not in use, the material should be kept in a tightly sealed bottle and stored in a cool, dark place.

Material of this kind is intrinsically heterogeneous. Consequently, the analyst should endeavor to minimize any segregation by thoroughly mixing the contents of the bottle by shaking and rolling before each use. In addition, when taking a portion for analysis, the analyst should strive to remove as representative a sample as possible.

Preparation and Analysis

This SRM was prepared from material dredged from the bottom of the Indiana Harbor Canal near Gary, Indiana. This material was screened to remove foreign objects, freeze dried, and sieved to pass a No. 80 ($180\mu\text{m}$) screen. This material was thoroughly mixed in a V-blender, bottled, and sequentially numbered. The material has been radiation-sterilized to minimize alteration from biological activity.

Randomly selected bottles were used for the analytical measurements. Each analyst examined at least 6 bottles, some of them measuring replicate samples from each bottle. No correlation was found between measured values and the bottling sequence. The results of measurements on samples from different bottles did not appear to differ significantly from sub-samples within the bottles. Accordingly, it is believed that all bottles of this SRM have substantially the same composition. The analytical methods employed were those in regular use at NBS for certification of Standard Reference Materials, except as noted below. Measurements and calibrations were made to reduce random and systematic errors to no more than one percent, relative. The uncertainties of the certified values listed in the table include those associated with both measurement and material variability. They represent the 95 percent tolerance limits for an individual sub-sample, i.e., 95 percent of the sub-samples from a unit of this SRM would be expected to have a composition within the indicated range of values 95 percent of the time.

The following values have not been certified because either they are not based on results of a reference method, or were not determined by two or more independent methods. They are included for information only.

All values are in units of $\mu\text{g/g}$ of sample, unless otherwise indicated.

Antimony	(51)	Potassium	(1.2 wt. %)
Arsenic	(66)	Scandium	(2)
Cobalt	(8)	Sodium	(0.55 wt. %)
Lanthanum	(9)		

The values listed below are based on measurements made in one laboratory, and are given for information only. While no reason exists to suspect systematic bias in these numbers, no attempt was made to evaluate such bias attributable to either the method or the laboratory. The method used for each set of measurements is also listed. The uncertainties indicated are two times the standard deviation of the mean.

Kjeldahl Nitrogen	(0.0797% \pm 0.0048)
Total Phosphorus	(.051% \pm .0014)
Loss on Ignition (800 °C)	(10.72% \pm .28)
Oil and Grease (Freon)	(1.71% \pm .26)
Chemical Oxygen Demand (Dichromate)	(149,400 mg/kg \pm 9,000)

The methods used are:

Total Phosphorus - ASTM Method E-350.

Chemical Oxygen Demand (Dichromate) - Standard Methods for the Examination of Water and Waste Water, 14th Edition (1975), Section 508, page 550.

Oil and Grease (Freon 113 Extraction) - ibid., Section 502, page 518.

The following values are not certified, but are given to describe the matrix of the material: SiO₂ - 51%; MgO - 4%; Al₂O₃ - 4%; CaO - 4%.

H. L. Rook supervised collection, freeze drying, and homogenization of the SRM. The following members of the staff of the NBS Center for Analytical Chemistry performed the certification measurements: T. J. Brady; E. R. Deardoff; L. P. Dunstan; M. S. Epstein; R. Filby; M. Gallorini; E. L. Garner; T. E. Gills; J. W. Gramlich; R. R. Greenberg; S. H. Harrison; G. J. Lutz; L. A. Machlan; E. J. Maienthal; T. C. Rains; H. L. Rook; T. A. Rush; and W. P. Schmidt.

The development work, preceeding the certification of the SRM, was supported by the Environmental Protection Agency under an Interagency Agreement.

(Signature) CONTRACTING CONSULTING OFFICE R

SPECIFICATIONS

Generator Columns for Polynuclear Aromatic Hydrocarbons

MATERIALS

Glass Beads (4000 grams) - Glassport M, 60-80 mesh, #8501-6304, Hewlett Packard Corp., Avondale Division

#316 Stainless Steel Tubing (400 meters) - 1/4 in (6.4 mm) OD., 4 mm ID.,

Fittings for Columns (all fittings, nuts, and ferrules, should be Swagelok 316 SS)

- a. Porous Teflon Plugs (800) - approximately 4 mm diameter, but should be cut to fit snugly into 1/4 to 1/16 inch reducing union.
- b. 1/4 in. female nuts and ferrules (600)
- c. 1/4 to 1/16 in. reducing union (800)
- d. 1/4 to 1/16 in. reducing union with 5 micrometer (0.005mm) snubber (600)
- e. 1/16 in. cap. (600)

Chemicals (40 grams of each)

Anthracene, 1, 2 benzanthracene and 3,4 benzpyrene are to be used for coating three separate batches of glass beads. These compounds must be at least 98.5 mole % pure. 5 mg of each compound should be sent to NBS for a purity check.

Reagents - 70 liters methylene chloride, 50 liters methanol, 14 liters 1 % HF, 400 liters water. All organic solvents shall be reagent grade. The water used shall be distilled over alkaline permanganate.

Sieve - No. 45 U.S. Standard Sieve or equivalent (0.0139 in = 354 μ m opening)

PREPARATION OF GENERATOR COLUMNS

Description of Columns

720 stainless steel columns shall be made. Each column shall be 50 cm in length and have an internal diameter of 4 mm.

Cleaning Columns

The interior of each column shall be cleaned initially with soap and water and thoroughly rinsed. The columns should then be purged with 30 mL of methanol, methylene chloride and hexane respectively. All column fittings shall be cleaned by 5 minutes of ultrasonic agitation in methylene chloride.

Cleaning Beads

The beads shall be cleaned by 5 minutes of ultrasonic agitation in 14 liters of each of the following in succession: methylene

chloride, methanol, water, 1% hydrofluoric acid, water, and methanol respectively, discarding each solvent after agitation. The beads shall then be divided into three equal batches and stored in a clean glass container.

Coating Beads

Each batch of beads (one third of 14000g) shall be coated with a single polynuclear aromatic hydrocarbon (PAH) by immersing the beads in 10 liters of a 0.4% (wt/wt) solution of the PAH of interest dissolved in methylene chloride. The methylene chloride shall then be evaporated with a rotary evaporator.

After evaporation of the methylene chloride is complete, the residue shall be sieved with a #45 U.S. Standard Sieve to separate the coated beads from excess PAH compound. A sub sample of 10 grams of coated beads from each of the three batches shall be sent to NBS for analysis prior to packing columns.

Packing Columns

After receiving clearance from NBS, the coated beads of a single PAH shall be dry-packed into 240 of the previously prepared stainless steel tubes. Each column shall contain 15-16 grams of beads. One end of the column (inlet) shall be capped with a 1/4 to 1/16 inch reducing union that has been fitted with a porous Teflon plug. The opposite end shall be capped with a 1/4 to 1/16 inch reducing union that has been fitted with a 5 micrometer stainless steel frit (snubber).

Equilibrating Columns

Each column shall be thermostated at 50 °C and purged with 500 mL of distilled water. After equilibration, each end of the column should be fitted with a 1/16 inch Swagelok cap.

General Comments

Each of the three sieved batches of PAH coated glass beads must be coated with 0.3 to 0.5% of the respective compound. The columns for each of the three compounds shall be numbered according to the sequence of packing (1-240).



October 2, 1978

MEMORANDUM FOR Procurement Section

3X2 MC

From: W.E. May

Subject: Justification for Procurement of
Generators for Polynuclear Aromatic
Hydrocarbons (PAH)

Since many PAH are known to be carcinogenic or cocarcinogenic, there is justifiable concern regarding the measurement of extremely low concentrations of these compounds in water. The PAH generator columns, prepared as specified will be issued by NBS as an SRM. It will enable investigators to generate known, accurate concentrations (in the 1-50 ppb range) of a three, four, and five-condensed ring PAH in water, and use these certified concentrations for calibrating instrumentation and validating methodology.

BID LIST

1. Analabs
80 Republic Drive
North Haven, Conn. 06473
(203) 288-8463
Contact: Mr. William Cullen
2. Applied Science Lab.
P.O. Box 440
State College, Pa. 16001
(814)238-2406
Contact: Sharon McKinley
3. Waters Associates
Milford, Mass.
(617)478-2000
Contact: Ken Alden

SO-BCMB-ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND
ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

- 1 Develop Organic Standard Reference Materials for the
Calibration of Energy-Related Water Pollutant Measurement
Methods

No activity under this task in the present semi-annual report.

1 Develop Calibrated Radioactive Materials for Radiological Pollution Associated with Nuclear and Coal Energy Sources and Production

The goal of the program is to provide measurement traceability, through the U. S. Environmental Protection Agency at Las Vegas (EPA-LV), for certain radionuclides not included in other programs. These radionuclides were chosen because they are released into the environment from nuclear power reactors (such as light-water reactors), coal burning plants, or other, related, sources. The program for FY 76-80 is summarized in Table 25.

1.a Solution of Natural Isotopic Uranium, and Solution of Plutonium-241

The uranium oxide (UO_3) has been purified, solutions prepared and shipped to EPA. The isotopic composition of the uranium has been certified by mass spectrometry, and the total uranium concentration has been determined by isotope-dilution mass spectrometry. A copy of the Report of Calibration for this material is attached as Appendix VI.

The EPA-LV has received the ampoules and Reports of Calibration of the calibrated solution of plutonium-241. We are continuing to measure the half life of plutonium-241 by means of measurements of the Spontaneous of americium-241.

1.b Fly Ash from Coal Combustion

Fly ash from the combustion of eastern United States coal is being assayed for radium-226 and radium-228. Homogeneity tests of the radioactivity in SRM 1633, Trace Elements in Coal Fly Ash, have

TABLE 25

Radiological Pollutant Quality Assurance^a

Performing Agency: National Bureau of Standards

(E-AP ID No. 79 BCN)

[Revised Milestones as of June 1978]

Δ - due ; ▲ - completed

Task 1. Radiological calibrated radioactive materials					
	FY 76	FY 77	FY 78	FY 79	FY 80
	\$k	91	50	50	30
1.1 Establish lab facility		▲			
1.2 ²¹⁰ Po solution		▲			
1.3 ²²⁶ Ra soil,			▲		
Mixed gamma solution,			▲		
²³⁹ Pu solution			▲		
1.4 Mixed gamma soil			▲		
1.5 Natural U solution,			▲		
²⁴¹ Pu solution			▲		
1.6 Fly ash from coal ^b				Δ	
1.7 ²³² Th solution,				Δ	
Mixed radionuclide solution				Δ	
1.8 ²¹⁰ Pb solution,					Δ
²⁴³ Cm solution,					Δ
²⁴⁴ Cm solution					Δ

^a Issuances of all Standards are subject to satisfactory performance as defined by NBS Standard Reference Material criteria.

^b An additional \$31k was allocated for (i) traceability testing, which will be a continuing program, and (ii) preparation of the fly ash standard.

been performed by the Radioactivity Section and the material found to be satisfactorily homogeneous for this program. Ge(Li) gamma-ray measurements for the determination of radium-228 are in progress. Radon gas counting of radiochemically processed samples to determine the radium-226 concentration is nearing completion.

2 Measurement Tracability Studies with the Quality Assurance Branch of EPA-LV

The NBS conducts tests with the Quality Assurance Branch (QAB) to ascertain whether radioactivity measurements made by the QAB are traceable to NBS. These studies are on radioactive test sources, with known but undisclosed values, that are sent to the QAB by NBS, and on radioactivity standards prepared by QAB and sent to NBS for confirmatory measurements. The criteria for conducting the studies are given in an appendix to the NBS-EPA interagency agreement.

The status of these studies for this six-month period is given in Table 26. NBS has provided the QAB with six test sources of undisclosed value, and one result has been reported to NBS. A copy of the tracability statement for the completed test is attached as Appendix VII.

TABLE 26

Status of Traceability Studies of Radioactivity
Measurements by the Quality Assurance Branch (EPA-LV)
for the Period of July 1 through December 21, 1978

Test Sources Sent		Result Reported	
<u>Parent Radionuclide</u>	<u>Form</u>	<u>Radionuclide</u>	<u>QAB/NBS</u>
Cobalt-58	solution	Hydrogen-3	1.010
Strontium-89	solution		
Cerium-141	solution		
Lead-203	solution		
Uranium	solution		
Plutonium-238	point source		

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D.C. 20234

REPORT OF CALIBRATION

Uranium Solution of Natural Isotopic Composition
prepared for the
Quality Assurance Branch
U.S. Environmental Protection Agency
Las Vegas, Nevada

This solution consists of uranium of natural isotopic composition in approximately 4.9 g of 1 M HNO_3 in a flame-sealed borosilicate-glass ampoule.

The solution was prepared in the following manner. Uranium trioxide was dissolved in 4 M HNO_3 , uranium was precipitated as hydrated oxides from this solution with carbonate-free NH_4OH , and the precipitate was then dissolved in 4 M CH_3COOH . The uranium was purified in June 1978 by the method of Moore⁽¹⁾, starting with a solution of 1 M CH_3COOH containing 15 mg uranium per gram of acid. Uranium was next reprecipitated from 0.5 M HNO_3 with NH_4OH , and the precipitate was dissolved with 2 M HNO_3 . The final solution was prepared by filtering this solution, diluting it with water to 1 M in HNO_3 , and then adding 1 M HNO_3 until the desired uranium concentration was reached.

Six of the 315 ampoules containing aliquants of the final solution were assayed for uranium isotopic composition and total uranium concentration by isotopic dilution mass spectrometry⁽²⁾ in the Inorganic Analytical Research Division, National Bureau of Standards, in September 1978. Summaries of the results of these assays are given in Tables 1 and 2.

The radioactivity concentrations of ^{234}U , ^{235}U , and ^{238}U were calculated using the conversion factors and constants that are listed in Table 3. The calculated values are given in Table 4. The radioactivity concentration of each isotope is equal to its alpha-particle-emission rate per gram of solution, within the stated uncertainty.

For the Director,

W. B. Mann

W. B. Mann, Chief
Radioactivity Section
Center for Radiation Research

November 1978

TABLE 1. Summary of the Isotopic Composition^(a,b) and the Atomic Mass.

	<u>²³⁴U</u>	<u>²³⁵U</u>	<u>²³⁸U</u>
Atom percent	0.0052 ± 0.0002	0.7204 ± 0.0006	99.2743 ± 0.0008
Calculated mass percent	0.0051 ± 0.0002	0.7114 ± 0.0006	99.2835 ± 0.0008

Atomic mass of uranium = 238.0287 amu

a) The indicated uncertainties are composed of the linear sum of statistical error in the mass spectrometric measurements at the 95-percent confidence level and the sum of conceivable systematic errors.

b) Uranium-236 was not detected. An upper limit of 0.00005 atom percent was estimated on the basis of the noise-to-signal ratio.

TABLE 2. Uranium Concentration data^(a).

<u>Milligrams of U per gram of solution</u>	<u>Milligrams of ²³⁵U per gram of solution</u>	<u>Milligrams of ²³⁸U per gram of solution</u>
3.4776 ± 0.0035	0.02474 ± 0.00003	3.4525 ± 0.0035

a) The indicated uncertainties are composed of the linear sum of statistical error in the mass spectrometric measurements at the 95-percent confidence level and the sum of conceivable systematic errors.

TABLE 3. Relevant Conversion Factors and Constants.

Half life of ²³⁴ U = (2.445 ± 0.010) × 10 ⁵ y ⁽³⁾
Half life of ²³⁵ U = (7.038 ± 0.005) × 10 ⁸ y ⁽⁴⁾
Half life of ²³⁸ U = (4.468 ± 0.003) × 10 ⁹ y ⁽⁵⁾
Atomic mass of ²³⁵ U = (235.043925247 ± 0.000002552) amu ⁽⁶⁾
Atomic mass of ²³⁸ U = (238.050785782 ± 0.000002361) amu ⁽⁶⁾
Avagadro constant = (6.0220978 ± 0.0000010) × 10 ²³ ⁽⁷⁾
Length of tropical year = 3.155693 × 10 ⁷ s ^(a)

a) based on the ephemeris second.

TABLE 4. Calculated Isotopic Uranium Radioactivity Concentrations, October 1977

$^{234}\text{U} \text{ (s}^{-1}\text{g}^{-1}\text{)}$	$^{235}\text{U} \text{ (s}^{-1}\text{g}^{-1}\text{)}$	$^{238}\text{U} \text{ (s}^{-1}\text{g}^{-1}\text{)}$
$41.3 \pm 5.2\%$ (a)	$1.98 \pm 0.4\%$ (b)	$42.9 \pm 0.3\%$ (b)

- a) The indicated uncertainty is the linear sum of the uncertainty in the mass-percent value and three times the uncertainty in the half-life value.
- b) The indicated uncertainty is the linear sum of the uncertainty in the concentration value and three times the uncertainty in the half-life value.

References

- (1) F. L. Moore, "Liquid-Liquid Extraction of Uranium and Plutonium from Acetate Solution with Triiso-octylamine", Anal. Chem., 32(9), 1075 (1960).
- (2) E. L. Garner, L. A. Machlan, and W. R. Shields, Uranium Isotopic Standard Reference Materials, NBS Special Publication 260-27, National Bureau of Standards, Washington (April 1971).
- (3) Y. A. Ellis, "Nuclear Data Sheets for A=234", Nucl. Data Sheets, 21, 493 (1977).
- (4) M. R. Schmorak, "Nuclear Data Sheets for A=231, 235, 239", Nucl. Data Sheets, 21, 91 (1977).
- (5) Y. A. Ellis, "Nuclear Data Sheets for A=238", Nucl. Data Sheets, 21, 549 (1977).
- (6) A. H. Wapstra and K. Bos, "The 1977 Atomic Mass Evaluation, Part I. Atomic Mass Table", Atomic and Nucl. Data Tables, 19, 177 (1977).
- (7) Recent, unpublished value, National Bureau of Standards.

REPORT OF TEST

Hydrogen-3 Radioactivity Test Solution

prepared for the

Quality Assurance Branch, USEPA

Las Vegas, Nevada

This test solution consisted of approximately 5 grams of water containing hydrogen-3. The solution was contained in a flame-sealed borosilicate-glass ampoule.

Material from another aliquot of this test solution was quantitatively diluted with triple-distilled water and the radioactivity concentration of hydrogen-3 in the dilute solution was determined by liquid-scintillation counting. Ten vials prepared from this material were intercompared with ten vials prepared from NBS Standard Reference Material 4926.

The radioactivity concentration of hydrogen-3 in this test solution, as of 0700 EST April 19, 1978, was

$$*1.748 \times 10^5 \text{ s}^{-1}\text{g}^{-1} \pm 2.8\%.$$

The total uncertainty in the radioactivity concentration value, 2.8 percent, is the linear sum of 0.2 percent, which is the limit to the random error of the liquid-scintillation comparative measurements at the 99-percent confidence level ($2.6 S_m$, where S_m is the standard error computed from 6 sets of 20 measurements), 2.5 percent, which is the uncertainty associated with SRM 4926, and 0.1 percent, which is a contribution to the uncertainty due to source preparation.

A half life of 12.35 ± 0.01 years [ORNL/NUREG/TM-102, 19, August, 1977] was used for the decay correction. The estimated systematic error given above includes a 0.8-percent contribution due to the uncertainty in the half life and the 16.62-year decay.

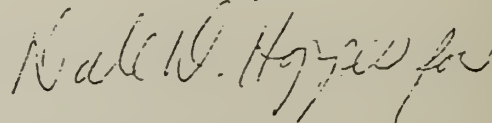
The Quality Assurance Branch of the U.S. Environmental Protection Agency (EPA) measured the radioactivity concentration of this solution by means of comparative liquid-scintillation measurements, and found it to be, as of 0700 EST April 19, 1978,

$$1.767 \times 10^5 \text{ s}^{-1}\text{g}^{-1} \pm 5.6\%.$$

The uncertainty in the EPA value, 5.5 percent, is the linear sum of 0.3 percent, which is the limit to the random error of the liquid-scintillation measurements at the 99-percent confidence level ($3.250 S_m$, where S_m is the standard error computed from 10 determinations), and 5.3 percent, which is the estimated upper limit of conceivable systematic errors.

The ratio of the EPA to NBS values, 1.010, demonstrates traceability of the EPA to NBS to within 1.0 percent as of April 1978, and lies within 5 percent of the NBS value as specified in the Appendix "Traceability Studies" of the NBS-EPA Interagency Agreement of April 20, 1976.

For the Director,

A handwritten signature in cursive script, appearing to read "W. B. Mann", followed by a flourish.

W. B. Mann, Chief
Radioactivity Section
Center for Radiation Research

August 15, 1978

